



COATINGS FOR DIRECTIONAL EUTECTICS

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Final Report

M. R. Jackson

J. R. Rairden

L. V. Hampton

Metallurgy and Ceramics Laboratory
Research and Development Center
General Electric Company
Schenectady, New York 12301

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Project Manager: John Merutka

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16. Abstract <p>Seven coating compositions were evaluated for oxidation protection of directionally solidified composite alloy NiTaC-13. These coatings included three NiCrAlY compositions (30-5-1, 25-10-1 and 20-15-1), two FeCrAlY compositions (30-5-1 and 25-10-1), a CoCrAlY composition (25-10-1), and one duplex coating, Ni-35Cr + Al.</p> <p>Duplicate pin samples of each composition were evaluated using two cyclic furnace oxidation tests: 100 hours at 871° C and 500 hours at 1093° C. The two best coatings were Ni-20Cr-15Al-1Y and Ni-35Cr + Al. The two preferred coatings were deposited on pins and were evaluated in detail in .05 MACH cyclic burner rig oxidation to 1093° C.</p> <p>The NiCrAlY coating was protective after 830 hours of cycling, while the duplex coating withstood 630 hours. Test bars were coated and cycled for up to 500 hours. Tensile tests indicated no effect of coatings on strength. In 871° C air stress rupture, a degradation (<1 Larson Miller parameter) was observed for coated relative to bare material. In 1093° C air stress rupture, the cycled NiCrAlY coating offered excellent protection with properties superior to the bare cycled NiTaC-13.</p> <p>The duplex coating offered little improvement over uncoated material once stress was applied. Ni-20Cr-15Al-1Y is a superior coating to Ni-35Cr + Al when applied to NiTaC-13.</p>					
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FOREWORD

This report describes results of work sponsored by the National Aeronautics and Space Administration from March 27, 1973, to December 27, 1973, under Contract NAS 3-16793, Mr. John Merutka, Project Manager, and was prepared by the Corporate Research and Development, General Electric Company, Schenectady, New York.

Also included in this report is additional work sponsored exclusively by the General Electric Company in areas that are of interest to the current effort but not within the scope of this contract. Specifically, results of stress-rupture tests regarding as-solidified, thermally cycled, and vacuum cycled NiTaC-13 and subsequent metallographic analyses are included.

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UNIT CONVERSION TABLE

S.I. units are used throughout the report. Tables and Figures (where possible) have S.I. units with standard American units in parentheses. In the text, only S.I. units are shown. The conversions for commonly encountered values are listed below. The principal measurements were taken with instruments calibrated in American units, except for weight, which was measured directly in milligrams.

	S.I.	American
Linear measure	0.00254 cm	0.001 inch
	0.075 cm	0.030 inch
	0.11 cm	0.045 inch
	0.15 cm	0.060 inch
	0.635 cm	0.250 inch
Temperature	760°C	1400°F
	871°C	1600°F
	927°C	1700°F
	982°C	1800°F
	1093°C	2000°F
Stress	689 MN/m ²	100.0 ksi
	345 MN/m ²	50.0 ksi
	138 MN/m ²	20.0 ksi

SUMMARY

In Task I of this study, seven coating compositions were evaluated for providing oxidation protection to the directionally solidified composite alloy NiTaC-13. These coatings included three NiCrAlY compositions (30-5-1, 25-10-1 and 20-15-1), two FeCrAlY compositions (30-5-1 and 25-10-1), and one duplex coating, Ni-35Cr + Al. These seven coatings were deposited onto pin substrates at three temperatures: 700°, 850°, and 1000°C. The samples were evaluated metallographically, and the condition giving the most adherent and fissure-free coating for each composition was selected for further evaluation. Pin samples of each coating deposited using the preferred conditions were post-coating heat treated in argon at two conditions: 3 hours at 1160°C and 1 hour at 1230°C. The 1160°C heat treatment was selected for all compositions in order to minimize the coating-substrate interaction effects.

Finally, duplicate pin samples of each composition were evaluated using two cyclic furnace oxidation tests: 100 hours at 871°C and 500 hours at 1093°C. The two best coatings selected for Task II were Ni-20Cr-15Al-1Y and Ni-35Cr + Al.

In Task II, the two preferred coatings were deposited on pins and were evaluated in detail in cyclic burner rig oxidation. The burner rig operated on JP-5 jet engine fuel at 0.05 Mach. The cycle was approximately one hour long, from 93° to 1093°C, with the majority of the cycle at 1093°C. The NiCrAlY coating was protective after 830 hours of cycling, while the duplex coating withstood 630 hours. NiTaC-13 definitely needs a protective coating, since a 0.25 cm dia. uncoated pin lost half the starting weight in 200 hours. In burner rig cycling, little microstructural change occurred in the coating, but metallurgical instability was observed in the substrate and at the coating-substrate interface. A platelet phase developed in the substrate, and fiber denudation was seen where substantial interaction of coating and substrate occurred.

Based on the pin sample exposures, test bars were coated and burner rig cycled for 150 and 500 hours for NiCrAlY and 150 and 250 hours for the duplex coating. Tensile tests at room temperature, 871°C and 1093°C indicated no detrimental effect of coatings on strength, although a slightly lower room temperature ductility was observed.

Burner rig cycled bars with either coating exhibited less than one Larson Miller parameter loss relative to bare cycled material in air stress-rupture tests at 871°C. In 1093°C air stress rupture tests, the duplex coated cycled bars were equivalent to bare cycled bars, while the NiCrAlY coated cycled bars were a parameter better than bare cycled bars. In fact, the NiCrAlY coated bars were equivalent to vacuum cycled NiTaC-13 tested in argon. It should be noted that NiTaC-13 suffers on the order of a one-parameter loss in stress rupture properties for cycled relative to uncycled material. This is likely due to the metallurgical instabilities noted in the microstructure.

Ni-20Cr-15Al-1Y is a superior coating to Ni-35Cr + Al when applied to NiTaC-13. Denudation of fibers in the substrate close to the coating appeared to be a minor problem for mechanical behavior of 0.254 cm diameter bars, but the effect may be of major importance in thinner wall (approximately 0.1 cm) turbine blade sections.

INTRODUCTION

Directionally solidified eutectic alloys are being considered as possible jet engine turbine blade materials. (1) Because their highly aligned microstructures are formed during solidification, they offer potential structural stability and property retention to a greater fraction of their solidification temperatures than do other materials.

To ease the transition from present alloys to aligned eutectics, it seems desirable from a design standpoint to find eutectics which have characteristics similar to, but improved over, conventional alloys. The most advanced eutectic alloy designed by the General Electric Company Aircraft Engine Business Group (AEBG) to approach this goal is NiTaC-13. The melt composition from which this eutectic alloy is grown is Ni-3.3Co-4.4Cr-3.1W-5.4Al-5.6V-6.2Re-8.1Ta-0.54C (in weight percent). (2) Transverse and longitudinal views of the aligned microstructure are shown in Figure 1. The brightest phase is the monocarbide fiber formed at solidification, (Ta,V)C. The fibers are approximately 1 μ m in cross-section and are 2-3 volume percent of the microstructure. The darkest phase is γ' , the face centered cubic ordered structure based on Ni₃Al. This phase precipitates from the austenitic γ matrix during the cool-down following solidification. It is present as basically cubic particles, about 1 μ m on a side. Relative to the surrounding f. c. c. γ network, the γ' phase is enriched in Al, Re, Ta, and W and poor in Cr and V.

For alloys similar in composition to NiTaC-13, the f. c. c. fiber and γ have a common growth axis, $\langle 100 \rangle$, and $\{110\}_{TaC} \parallel \{110\}_{\gamma} \parallel \gamma-TaC$ interface. (3, 4) From longitudinal and transverse sections, it can be found that the cube faces of the γ' precipitate are $\{100\}$ planes and are parallel to the same plane in the γ matrix.

Unlike conventional superalloys containing 15-20 w/o Cr, NiTaC-13 contains only 4.4 w/o Cr. As might be expected, the alloy exhibits poor oxidation resistance. (5) To maintain surface integrity at maximum metal service temperatures approaching 1100°C, this alloy and similar future modifications will require a protective coating.

The objective of this program has been to develop an environmentally stable coating for NiTaC-13. The approach used was to deposit coatings 7.6 - 10.2 $\times 10^{-3}$ cm (3-4 mils) thick by vacuum evaporation from an electron beam heated source onto pin and test bar specimens. During Task I of this study, screening tests were performed on seven coating alloys with the following nominal compositions:

- Ni-25Cr-10Al-1Y
- Ni-30Cr- 5Al-1Y
- Ni-20Cr-15Al-1Y
- Fe-30Cr- 5Al-1Y
- Fe-25Cr-10Al-1Y
- Co-25Cr-10Al-1Y
- Ni-35Cr plus Al

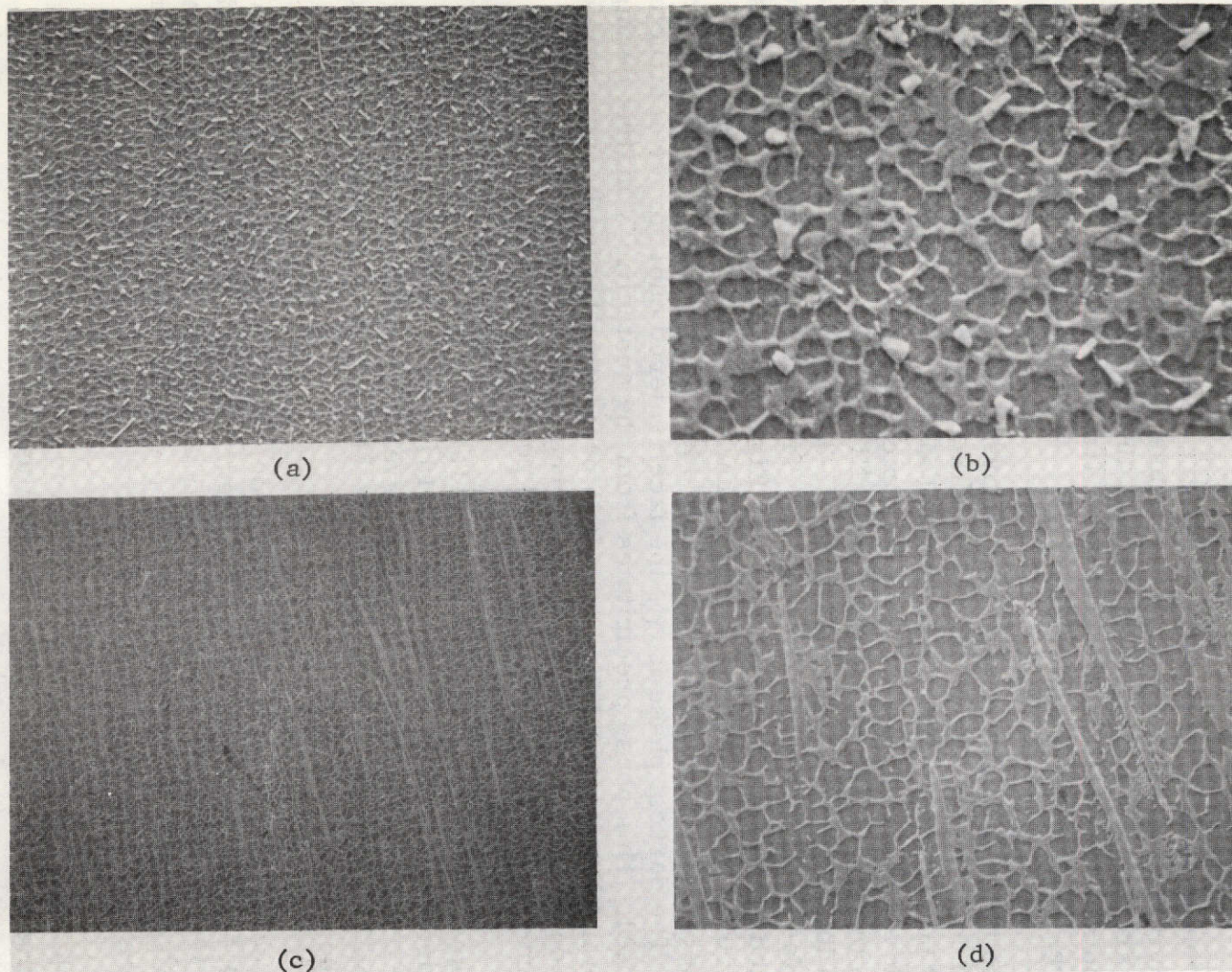


Figure 1 Scanning electron micrographs of as-directionally solidified NiTaC-13:
 (a) transverse, 602X, (b) transverse, 2580X, (c) longitudinal, 602X,
 (d) longitudinal, 2580X.

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Pin samples of each composition were coated at substrate temperatures of 700°, 850°, and 1000°C. Metallographic examinations of each of these samples were made, and the preferred deposition temperature for each composition was determined on the basis of good coating-to-substrate adhesion and comparative absence of flaws in the coatings.

The preferred deposition conditions were:

Ni-25Cr-10Al-1Y; 1000°C	Fe-25Cr-10Al-1Y; 1000°C
Ni-30Cr- 5Al-1Y; 1000°C	Co-25Cr-10Al-1Y; 700°C
Ni-20Cr-15Al-1Y; 1000°C	Ni-35Cr plus Al; 700°C
Fe-30Cr- 5Al-1Y; 850°C	

Samples of each of the coatings deposited using the preferred deposition temperature were heat treated at 1160°C for 3 hours and 1230°C for 1 hour. It was decided to use the 1160°C heat treatment for all of the compositions to minimize interdiffusion effects between the coatings and the NiTaC-13.

Duplicate pin samples of each of the compositions were prepared by deposition at the preferred temperatures and heat treatment at 1160°C. These were subjected to a cyclic oxidation test to evaluate their relative oxidation resistance and stability. The preferred compositions selected for Task II were:

Ni-20Cr-15Al-1Y
Ni-35Cr plus Al (duplex coating)

For Task II, pin samples, stress-rupture bars and tensile bars were coated with the preferred compositions. These samples were placed on the 1093°C burner rig at AEBG, Lynn, Mass. The pin samples were used to evaluate the oxidation rate of the compositions under burner rig conditions with cycling to room temperature to simulate a jet engine cycle. This rate was used as a guide in selecting exposure times for the Ni-20Cr-15Al-1Y and Ni-35Cr + Al coated test bars.

After cyclic burner rig exposure, duplicate test bars were evaluated using the following conditions: (1) stress-rupture tests at 871°C (434-482 MN/m²) and 1093°C (103-138 MN/m²); and (2) tensile tests at room temperature, 871°C and 1093°C.

MATERIALS AND TEST SPECIMENS

Ingots of the source alloys were prepared by induction melting high purity metals in a low pressure, non-oxidizing environment, then casting the alloys in an argon atmosphere. A section was cut from an ingot and placed in the water-cooled crucible to serve as the evaporation source. Previous experience has shown that a nearly steady state vapor composition is reached using MCrAlY-type sources under the conditions of these experiments after the equivalent of one deposition run ($7.6 - 10.2 \times 10^{-3}$ cm on rotating substrates located approximately 10.2 cm from the source). Hence, the coatings in this study were deposited after the source ingot had been so conditioned.

The samples used for this study were directionally solidified NiTaC-13 pins 4.45 cm long and 0.254 cm in diameter. All NiTaC-13 for this study was melted with an R.F. (radio frequency) graphite susceptor system and solidified at 0.635 cm/hour. Prior to deposition, the pins were centerless ground and lightly abraded with alumina powder. One or two pins were mounted approximately 10.2 cm from the source in a specially designed motor driven rotating device which turns the pins at approximately 10 rpm during deposition. The pin temperature is controlled by use of a resistance heated refractory metal foil mounted behind the pins. The pin temperature was measured using a Pt/Pt-Rh thermocouple placed in a stainless steel tube (approximately the same mass as the pins), which was mounted in close proximity to the pins.

Pins were coated with $7.6 - 10.2 \times 10^{-3}$ cm of each of the seven of the compositions to be evaluated in Task I, using deposition temperatures of 700°, 850°, and 1000°C. The deposition rate was $0.38 - 0.51 \times 10^{-3}$ cm/min. A segment from each of the pins was examined metallographically, and the best processing condition for each composition was determined on the basis of: (1) the absence of flaws in the coating; and (2) the soundness (freedom from cracking or poor adhesion) of the bond at the coating-substrate interface. Following are comments which describe the microstructure of each sample; micrographs are presented which illustrate examples of good and poor coatings. (Micrographs of best deposited conditions plus post heat treatment are also included in the figures shown; these will be discussed in later sections of this report.)

<u>Composition</u>	<u>Comments</u>
Ni-35Cr(T) + Al (cold)**	
T = 700°C*	NiCr bonded well to substrate. No diffusion. Small diffusion between Al & NiCr. See Fig. 2a.
T = 850°C	Many fissures in NiCr as shown in Fig. 2b. Substrate bond good. Al bond good.
T = 1000°C	Good substrate bond with NiCr. Some fissures. Good Al deposit.
Fe-30Cr-5Al-1Y	
700 & 850°C*	Good bonding. Many fissures. No diffusion. See Fig. 3a.
1000°C	As above except small diffusion zone and fewer fissures.
Fe-25Cr-10Al-1Y	
700°C	Good bonding. Many fissures. Small diffusion zone.
850°C	Substrate bond good. Coating jagged and rough with many radial fissures. Small diffusion zone with second phase precipitation on substrate side of interface.
1000°C*	Good bonding with a large amount of two-way diffusion. No fissures. Second phase precipitation in diffusion zone on substrate side. Region ahead of diffusion zone appears slightly denuded. See Fig. 4a.

*The conditions selected for further evaluation.

**Aluminum deposited with no substrate heat.

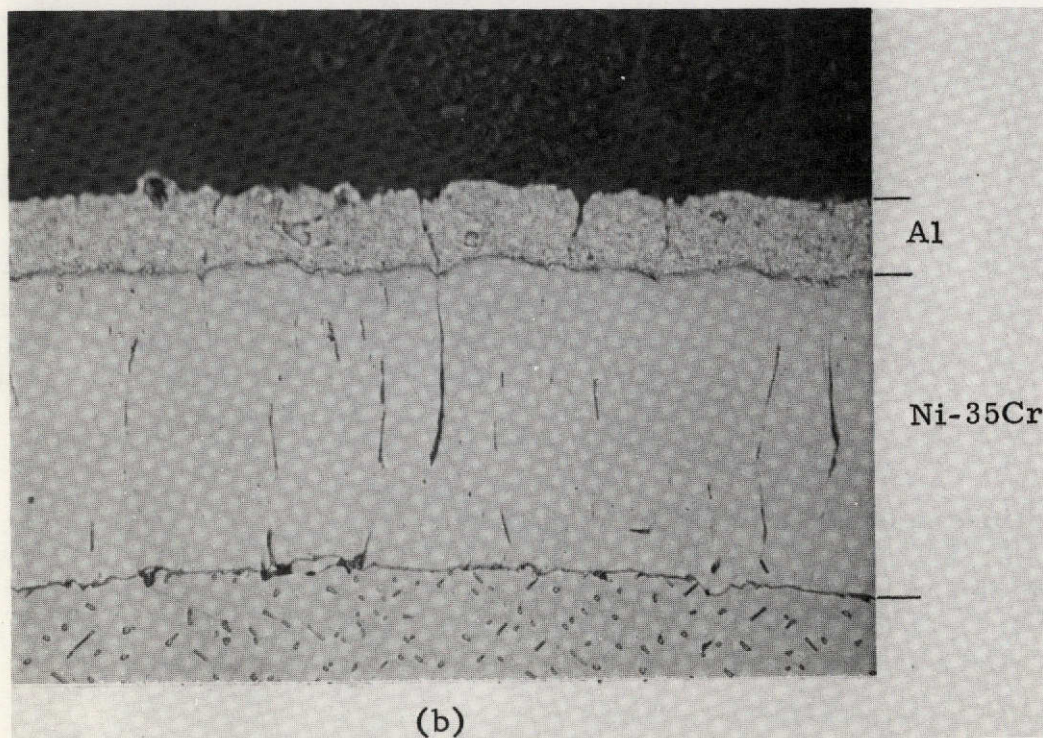
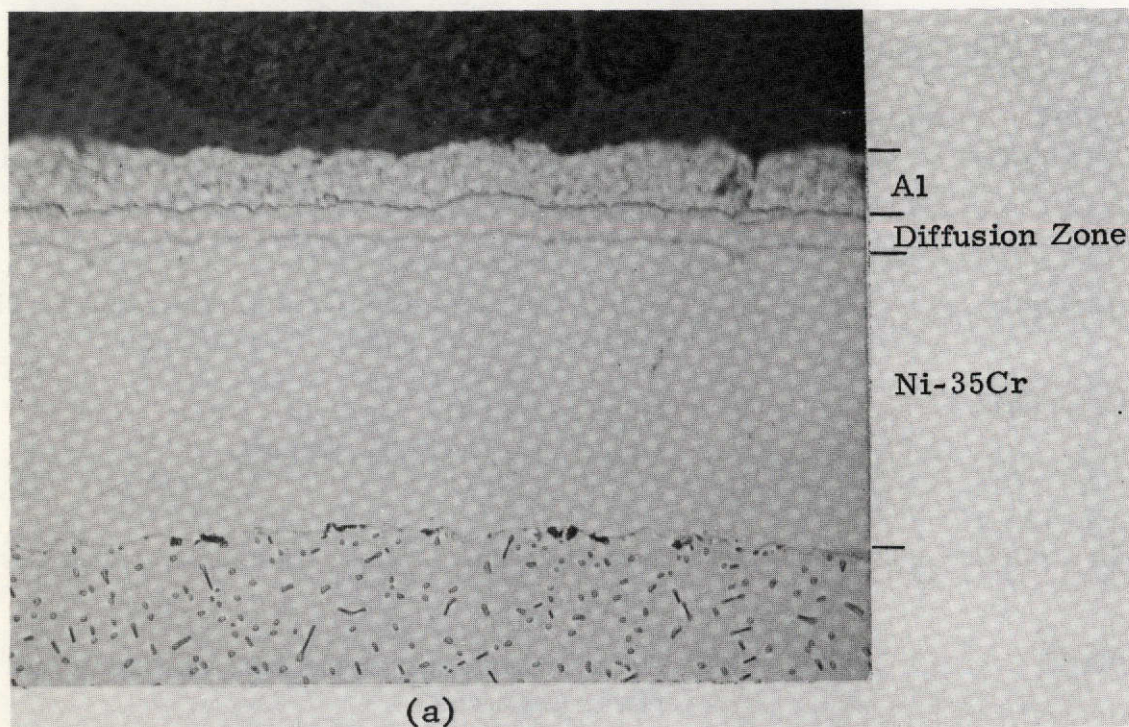


Figure 2 Ni-35Cr + Al on NiTaC-13. (a) As deposited at 700°C. (b) As deposited at 850°C; note fissures.

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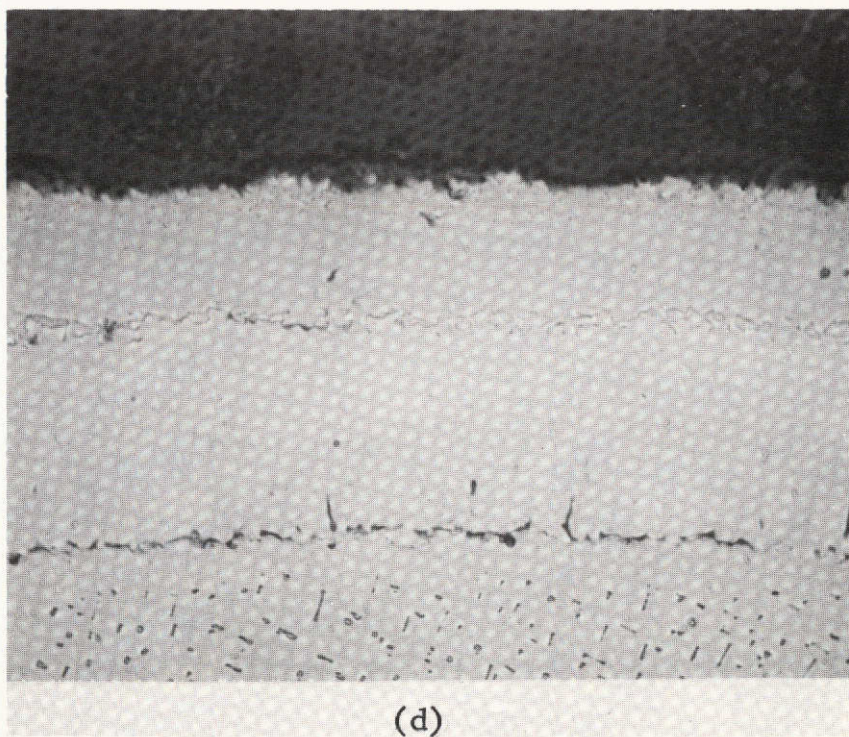
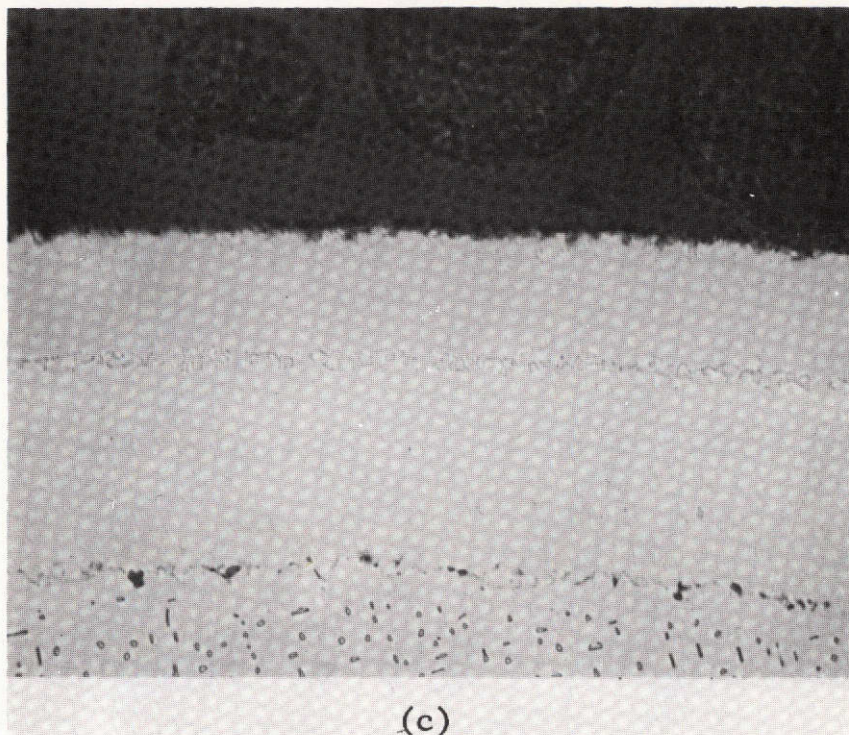


Figure 2 Ni-35Cr deposited at 700°C + Al on NiTaC-13. (c) As heat-treated for 3 hr at 1160°C in Ar. (d) As heat-treated for 1 hr at 1230°C in Ar.

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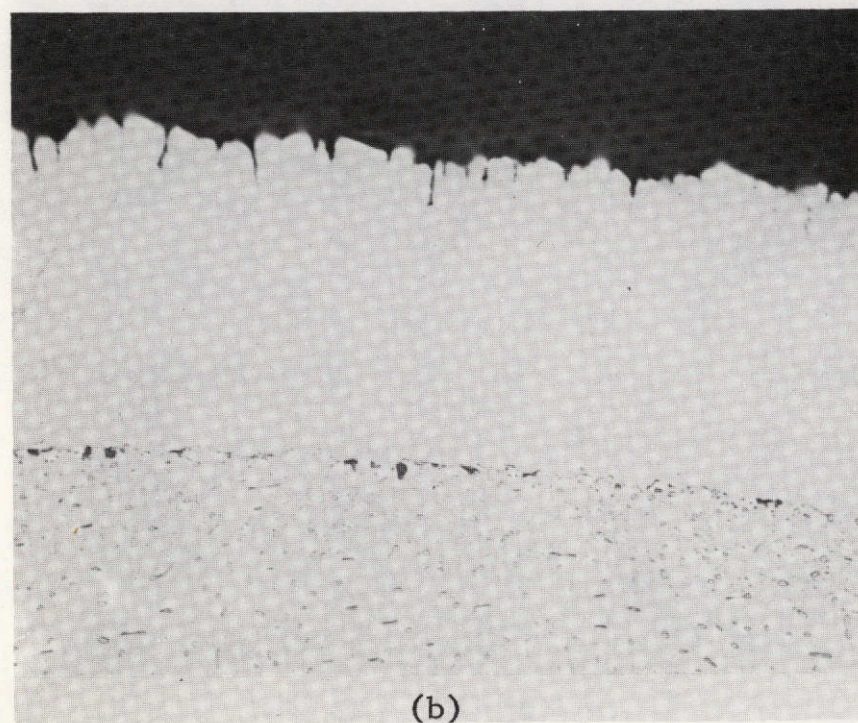
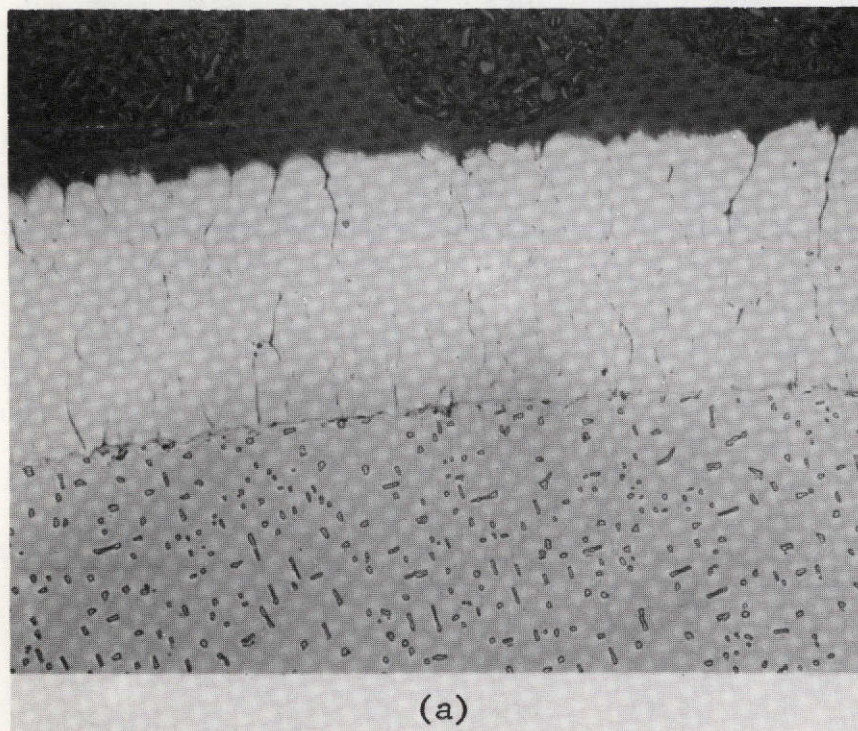


Figure 3 Fe-30Cr-5Al-1Y deposited at 850°C on NiTaC-13. (a) As deposited. (b) As heat-treated for 3 hr at 1160°C in Ar. 500X



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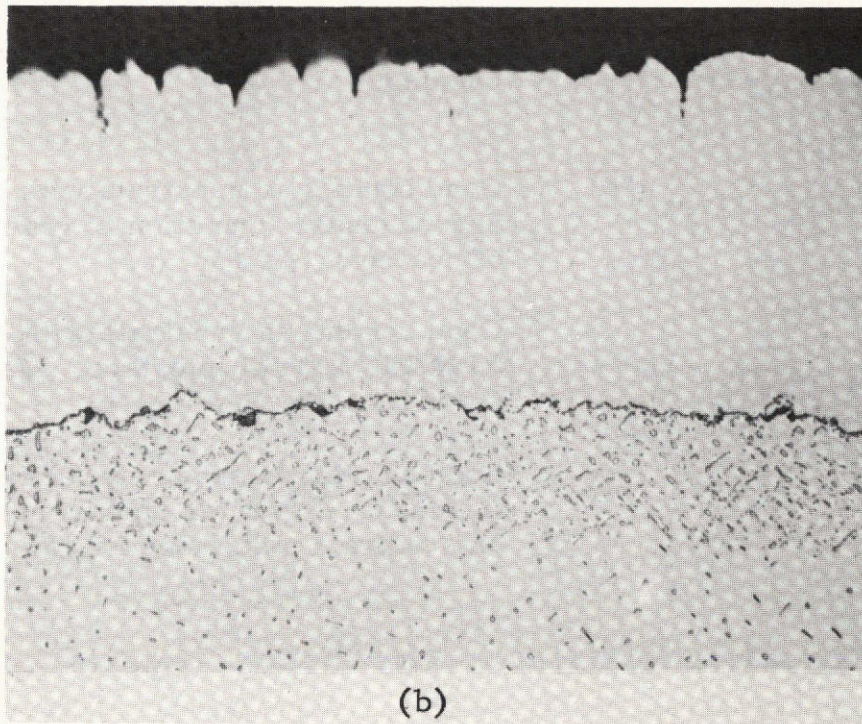
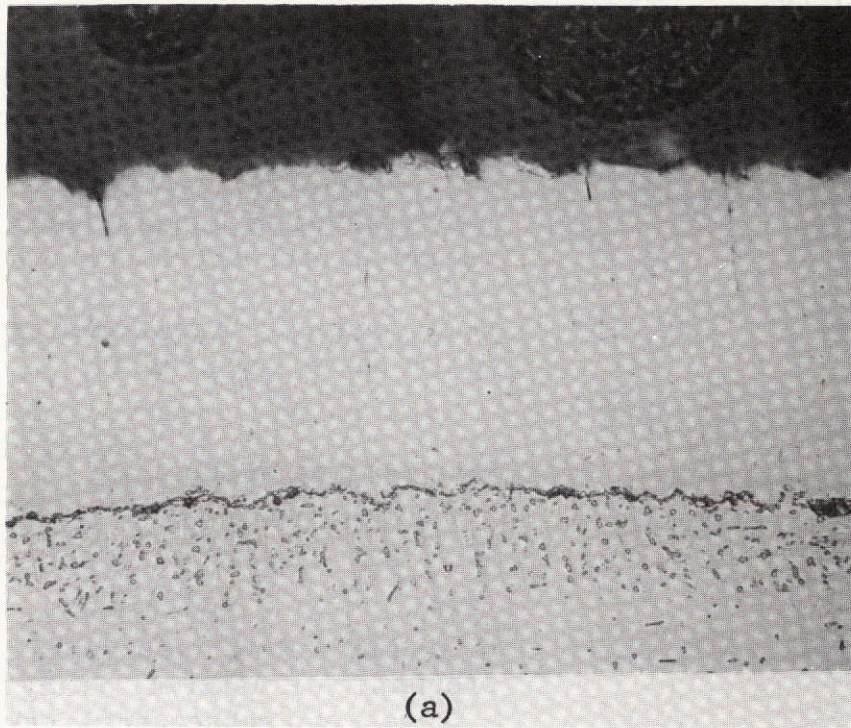


Figure 4 Fe-25Cr-10Al-1Y at 1000°C on NiTaC-13. (a) As deposited.
(b) As heat-treated for 3 hr at 1160°C in Ar.

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Ni-30Cr-5Al-1Y 700°C	Good bonding. Fissures extending the depth of coating in some places yet defect-free in others. This may be due to thermal expansion mismatch.
850°C	Good bonding with many fissures in coating but not as pronounced as above.
1000°C*	Good bonding with fewer fissures. Coating is two phase. See Fig. 5a.
Co-25Cr-10Al-1Y 700°C*	Good bonding to substrate. Many fissures, some traveling depth of coating. Coating is two phased (on etching). See Fig. 6a.
850°C	About 1/3 of coating non-adherent. Some breaks in coating itself indicating mismatch problem. Diffusion of coating material into substrate and subsequent breaking off below interface. Many fissures.
1000°C	Coating non-adherent. Breakage as above with a larger diffusion zone. Fig. 6b is an example of poor coating-to-substrate bonding.
Ni-20Cr-15Al-1Y 700°C	Good bonding to substrate with no diffusion. Second-phase formation in grain boundaries of coating. See Fig. 7a.
850°C	Good bonding to substrate with precipitation on NiTaC side of interface. Many radial fissures. See Fig. 7b.
1000°C*	Good bonding to substrate. Fewer radial fissures. A greater amount of precipitation on substrate side. See Fig. 7c.

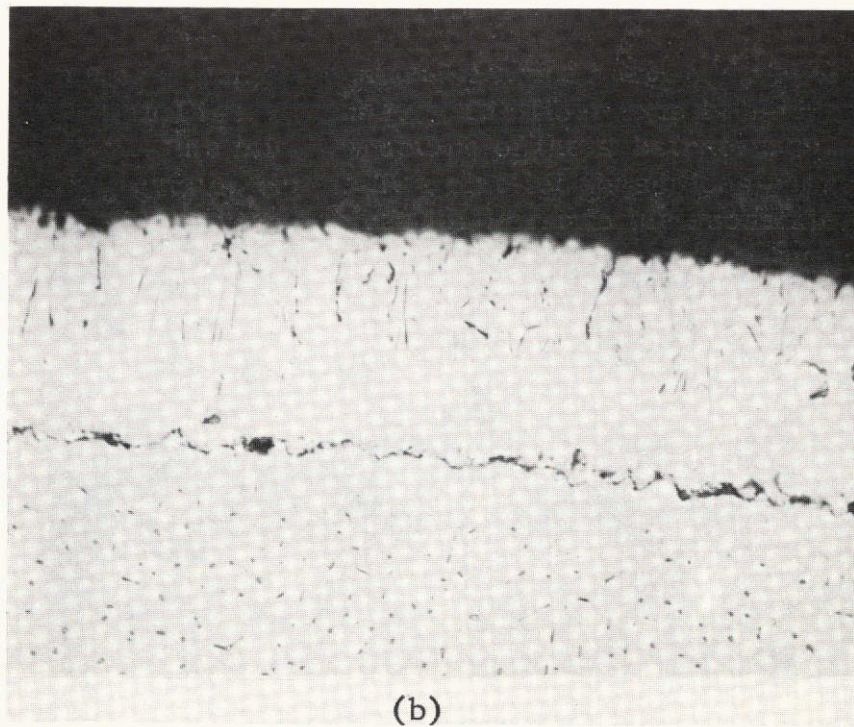
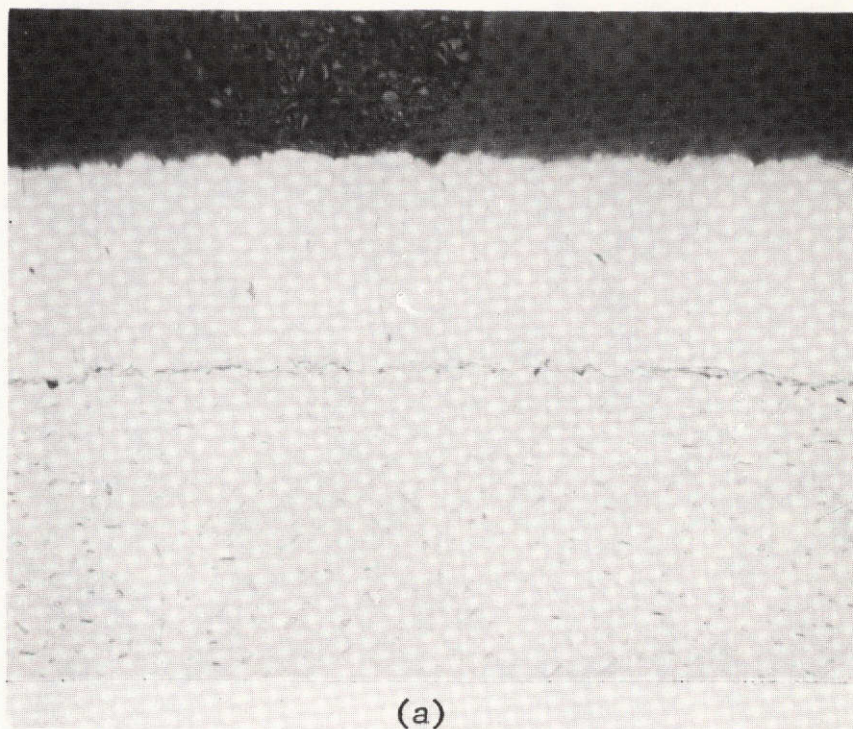


Figure 5 Ni-30Cr-5Al-1Y deposited at 1000°C. (a) As deposited. (b) As heat-treated for 3 hr at 1160°C in Ar. 500X

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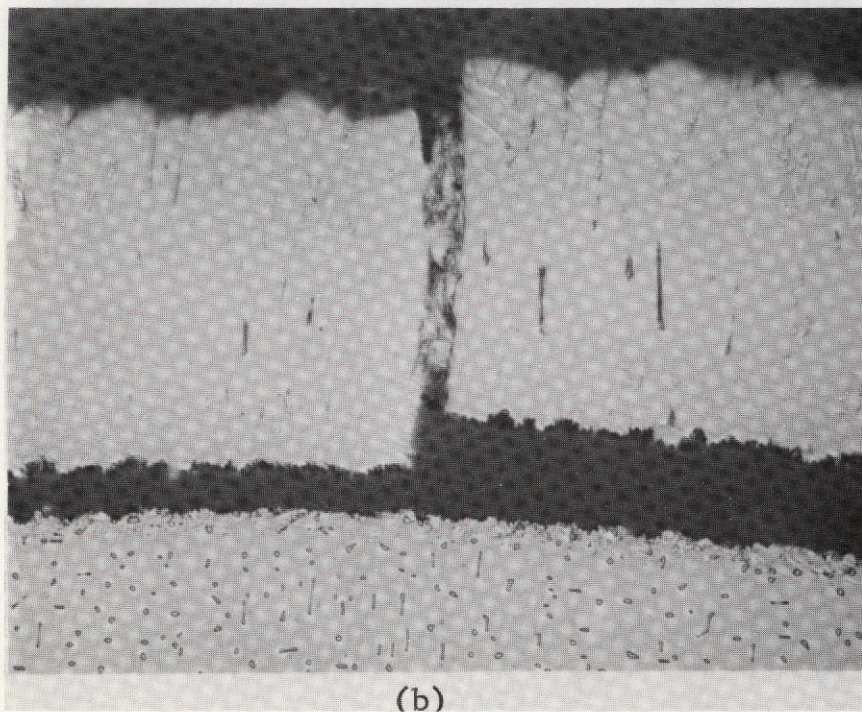
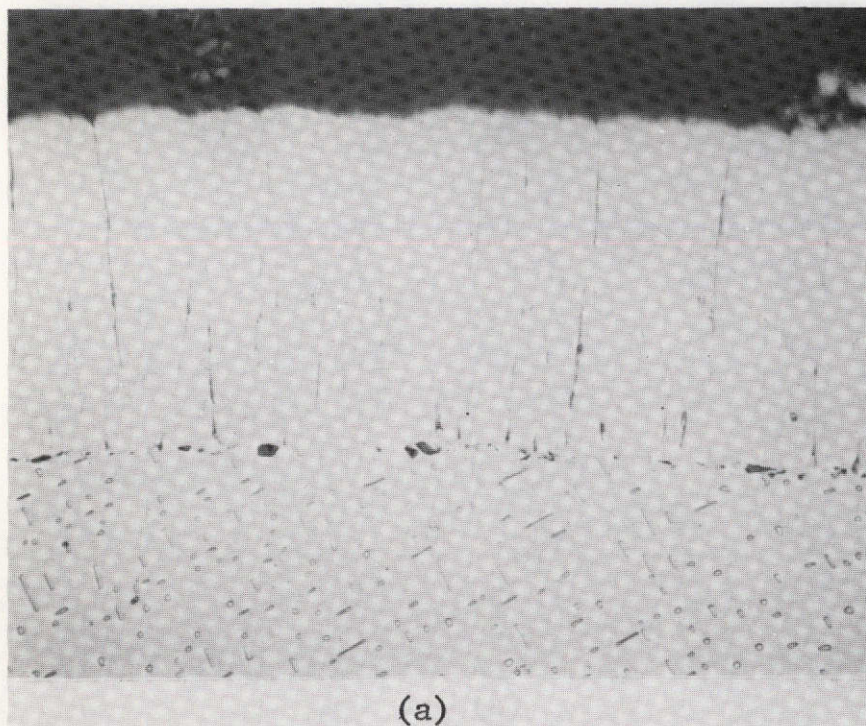


Figure 6 Co-25Cr-10Al-1Y on NiTaC-13. (a) As deposited at 700°C. (b) As deposited at 1000°C; note lack of coating-substrate adhesion. 500X

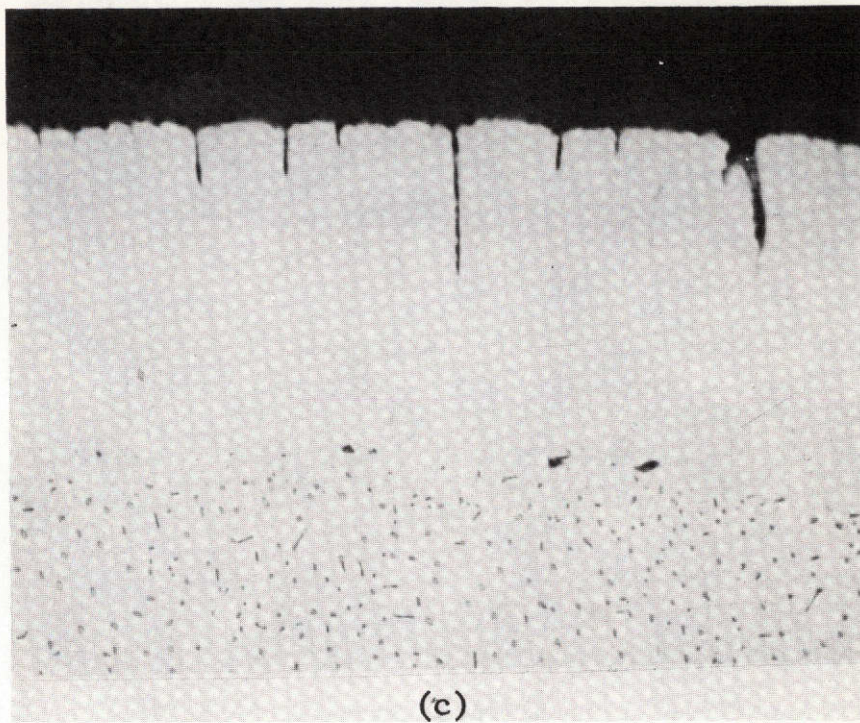
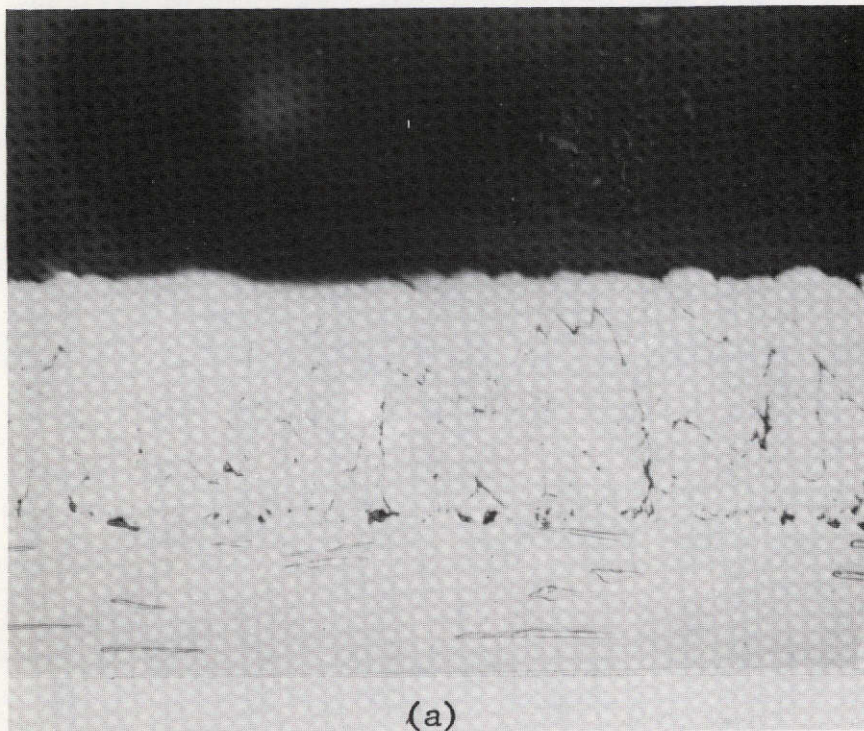
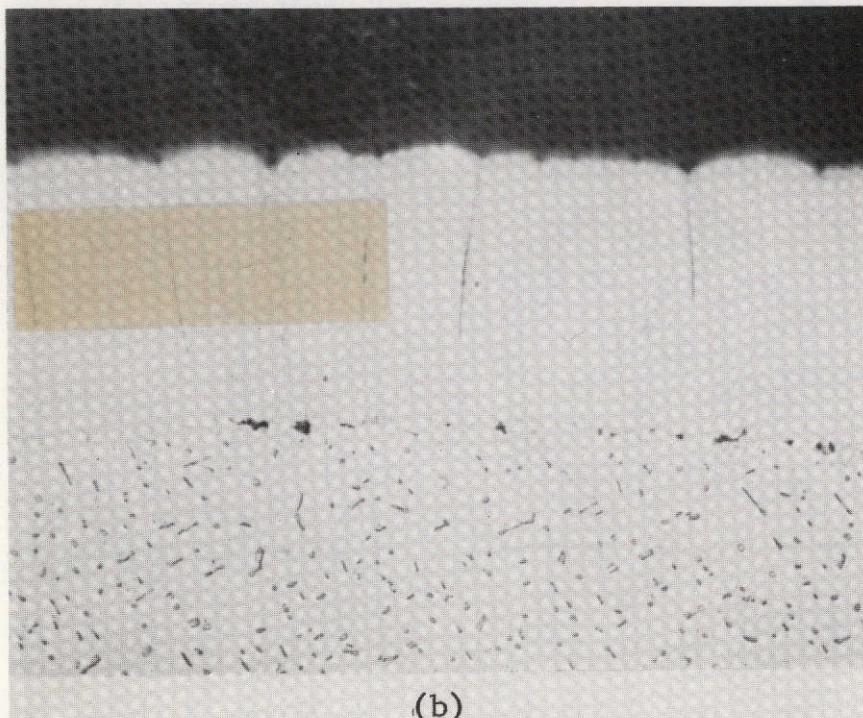


Figure 6 Co-25Cr-10Al-1Y on NiTaC-13. (c) Deposited at 700°C and heat-treated for 3 hr at 1160°C in Ar.
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(a)

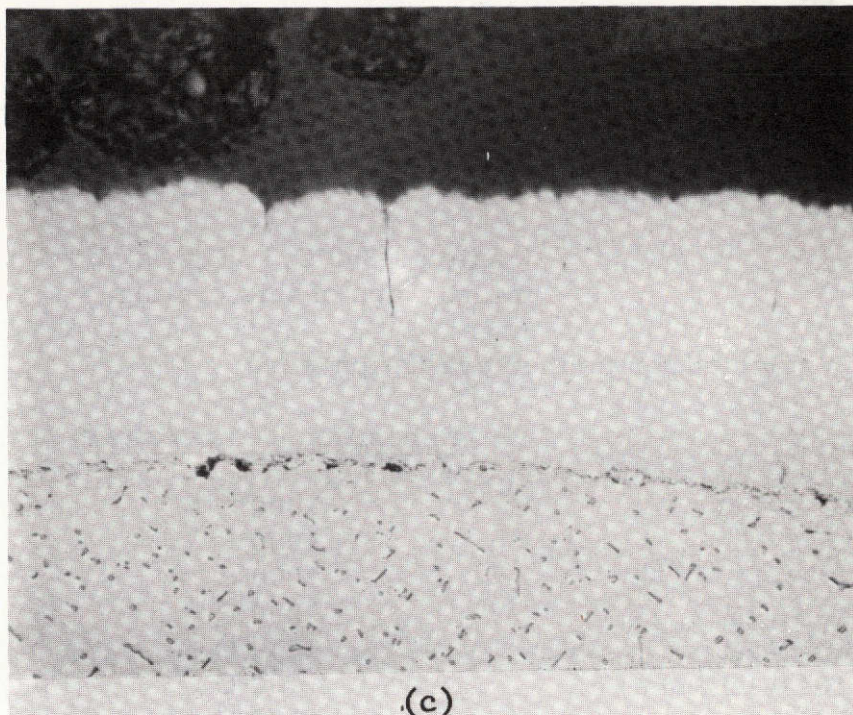


(b)

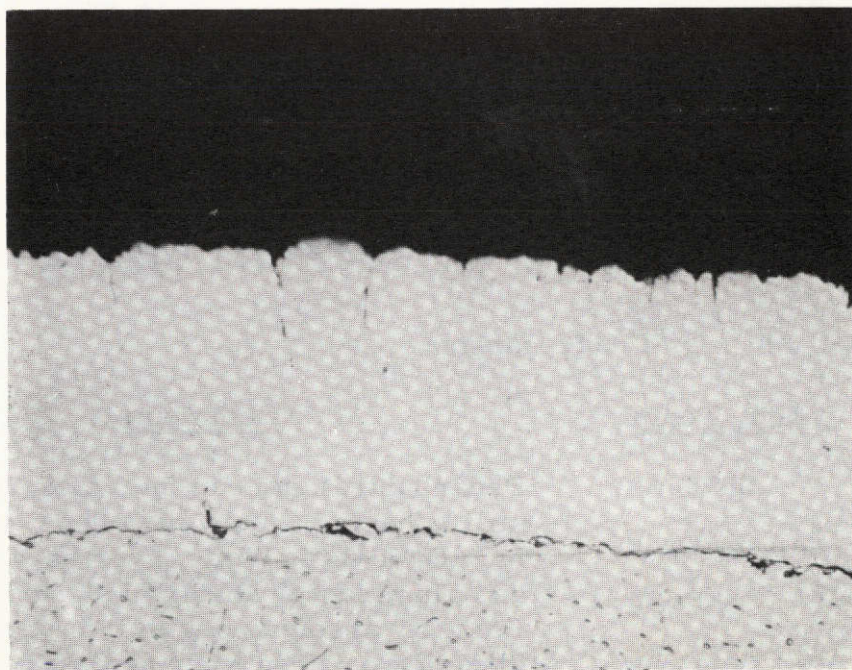
Figure 7 Ni-20Cr-15Al-1Y on NiTaC-13. (a) As deposited at 700°C.
(b) As deposited at 850°C.

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(c)



(d)

Figure 7 Ni-20Cr-15Al-1Y on NiTaC-13. (c) As deposited at 1000°C.

(d) Deposited at 1000°C and heat-treated for 3 hr at 1160°C in Ar. 500X

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Ni-25Cr-10Al-1Y	
700°C	Good Bonding. Many grains. No diffusion.
850°C	Fewer grains in places but more in others. Good bonding. Small amount of precipitation on substrate side of interface.
1000°C*	(Same as 850°C.) Fig. 8a shows a photo- micrograph of this coating.

*The conditions selected for further evaluation were:

<u>Composition</u>	<u>Deposition Temperature</u>
Ni-25Cr-10Al-1Y	1000°C
Ni-30Cr- 5Al-1Y	1000°C
Ni-20Cr-15Al-1Y	1000°C
Fe-30Cr- 5Al-1Y	850°C
Fe-25Cr-10Al-1Y	1000°C
Co-25Cr-10Al-1Y	700°C
Ni-35Cr + Al	700°C

HEAT TREATMENT OF COATINGS

A. Ni-35Cr + Al Coatings

An evaluation was made of the effect of heat treatment temperature on the Ni-35Cr + Al (duplex) samples. Slices 0.25 cm thick were cut from the 3 types of samples (Ni-35Cr deposited at 700°, 850°, and 1000°C). They were heat treated for 3 hr at 1160°C in argon and examined metallographically - the results are summarized below:

Heat treatment: 3 hours, 1160°C, argon

<u>Composition</u>	<u>Dep. Temp.</u>	<u>Comments</u>
Ni-35Cr + Al (Al deposited on unheated Ni-35Cr coated substrate)	700°C	Decarburization near interface. Coating still adhering. Very high density of twins in NiCr layer. White layer between NiCr and aluminum probably high-chrome phase. Porosity associated with this phase. Good diffusion between NiCr and Al layers. Al layer is two phased. A photomicrograph of this coating is shown in Fig. 2c.

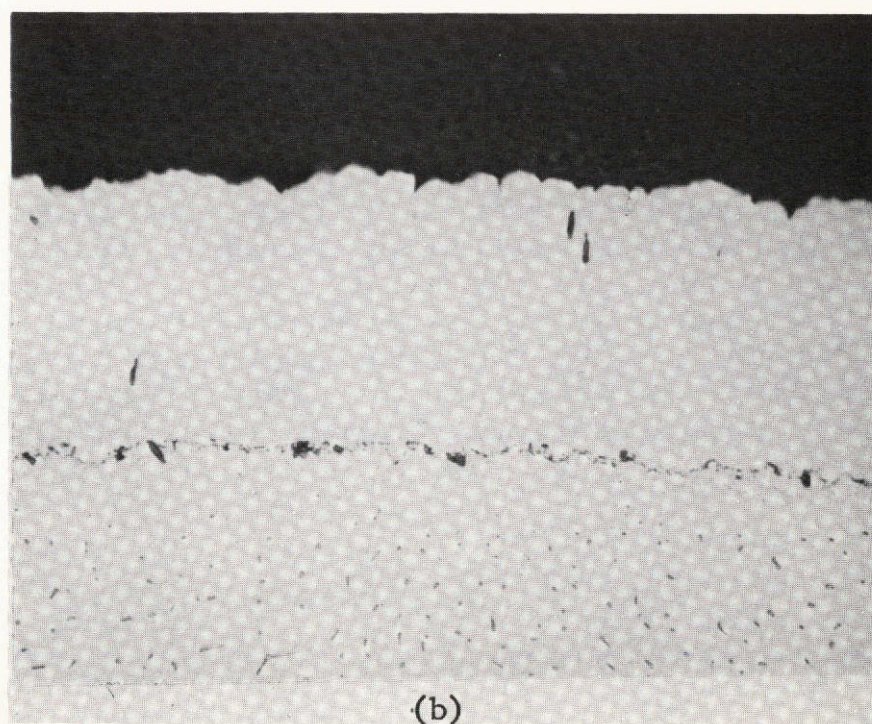
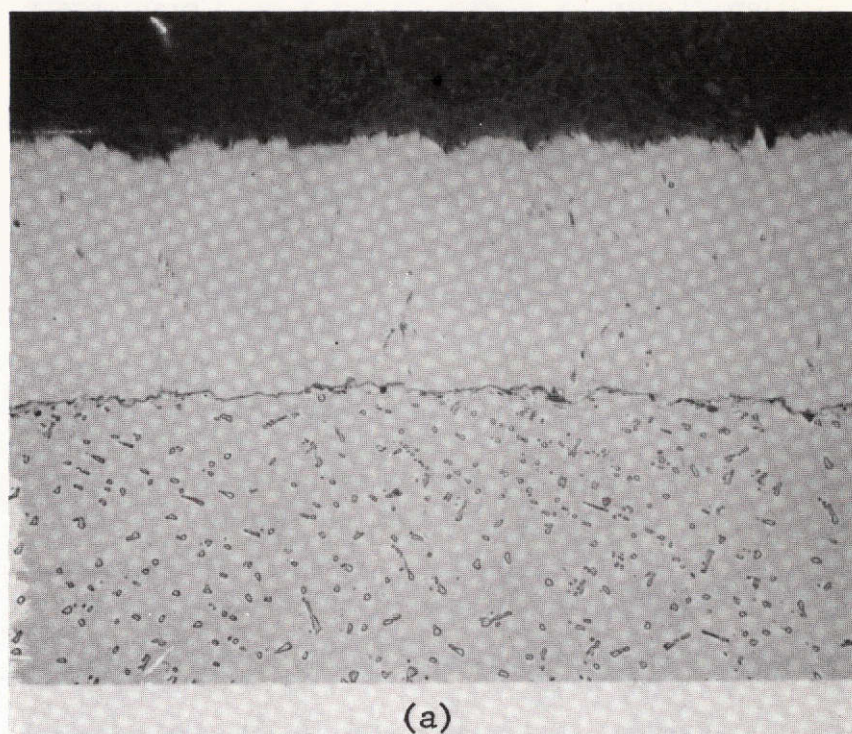


Figure 8 Ni-25Cr-10Al-1Y deposited at 1000°C on NiTaC-13. (a) As deposited. (b) As heat-treated for 3 hr at 1160°C in Ar. 500X

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<u>Composition</u>	<u>Dep. Temp.</u>	<u>Comments</u>
	850°C	Half of coating is unbonded. Where bonded, substrate region is denuded of carbides. White chromium-rich phase precipitating in grain boundaries of NiCr layer. Where separated, NiCr grains are heavily twinned. Good diffusion between Al and NiCr with second phase completely developed in Al layer.
	1000°C	Coating completely separated from substrate. Very little decarburization. White chromium-rich layer smaller. Second phase in Al-rich layer completely developed.

Heat treatment: 1 hour, 1230°C, argon

<u>Composition</u>	<u>Dep. Temp.</u>	<u>Comments</u>
as above	700°C	Morphology (Fig. 2d) is nearly identical to that of 700°C deposition temperature heat treated 3 hours at 1160°C in argon (Fig. 2c). Three zone coating. More fiber denuding of the substrate at the coating-substrate interface than seen at 1160°C.

B. MCrAlY Coatings

To arrive at a suitable heat treatment for the optimum as-coated condition, two heat treatments were selected based upon previous experience with CoCrAlY-type coatings: (1) a three-hour moderate temperature treatment, and (2) a one-hour relatively high temperature treatment. The temperatures decided on were 1160°C and 1230°C. Again 0.25 cm slices were cut from the coated pins and were placed into a furnace purged with argon. These samples were examined metallographically -- the results are summarized below:

Heat treatment: 3 hours, 1160°C, argon

<u>Composition</u>	<u>Dep. Temp.</u>	<u>Comments</u>
Ni-20Cr-15Al-1Y	1000°C	Few fissures. Some diffusion with second-phase precipitation on substrate side of interface. Two-phase coating. Slight decarburization. See Fig. 7d.

<u>Composition</u>	<u>Dep. Temp.</u>	<u>Comments</u>
Ni-30Cr-5Al-1Y	1000°C	Very few fissures. Two-way diffusion between substrate and coating with precipitation on substrate side of interface. Some decarburization. See Fig. 5b.
Fe-25Cr-10Al-1Y	1000°C	Large amount of two-way diffusion. Carbides appear affected by iron diffusion into substrate. Decarburization ahead of advancing diffusion interface. Few radial fissures in coating. See Fig. 4b.
Co-25Cr-10Al-1Y	700°C	At least two phases in coating with good distribution of secondary phase. Small diffusion zone between coating and substrate with second-phase precipitation. Carbides okay. See Fig. 6c.
Fe-30Cr-5Al-1Y	850°C	Coating surface rough and pitted. Few fissures. Large amount of coating diffusion. Decarburization ahead of diffusion zone. See Fig. 3b.
Ni-25Cr-10Al-1Y	1000°C	Few radial fissures. Two-phased coating. Secondary phase precipitation on substrate side of interface. Significant decarburization. See Fig. 8b.

Heat treatment: 1 hour, 1230°C, argon

<u>Composition</u>	<u>Dep. Temp.</u>	<u>Comments</u>
Ni-20Cr-15Al-1Y	1000°C	Few fissures. Two-phase coating. Precipitation of substrate side. Some decarburization.
Ni-30Cr-5Al-1Y	1000°C	Multiphased coating. Some amount of two-way diffusion. Large amount of decarburization.
Fe-25Cr-10Al-1Y	1000°C	Diffusion into substrate great. Denuded ahead of advancing diffusion zone but precipitates in zone.
Co-25Cr-10Al-1Y	700°C	Many fissures. Very small amount of diffusion. No decarburization. Two-phase coating.

<u>Composition</u>	<u>Dep. Temp.</u>	<u>Comments</u>
Fe-30Cr-5Al-1Y	850°C	Large amount of coating diffusion into substrate with denuded region ahead of advancing zone. Many fissures, some extending the depth of the coating.
Ni-25Cr-10Al-1Y	1000°C	Fissures closing and not many. Fair sized denuded region in substrate. Small diffusion into coating.

The heat treatment selected for all compositions was 1160°C for 3 hours.

FURNACE AND BURNER RIG EXPOSURE OF COATED SPECIMENS

A. Cyclic Oxidation Tests

Duplicate pin samples (0.254 cm dia) were coated and heat treated using the preferred conditions already described. These pins were mounted in a holder and subjected to the 100-hour, cyclic oxidation test at 871°C. This involved inserting the pins into a preheated static air furnace for 50 minutes, then removing them for a 10-minute air cool to approximately 93°C.

Another set of duplicate pin samples was coated for the second cyclic oxidation test which was performed at 1093°C for 500 hours under the same cycling conditions. In both tests, temperatures were constantly monitored by a thermocouple and chart recorder.

Following are the results of metallographic examination of these samples:

Cyclic Furnace Oxidation: 100 hours, 871°C

<u>Composition</u>	<u>Comments</u>
Fe-30Cr-5Al-1Y	Macro indicates coating integrity maintained. Micro supports this; however, there is some oxidation radially down the coating. Carbides near the coating interface are starting to break up.
Fe-25Cr-10Al-1Y	This coating was beginning to break up and spall. Micro revealed that oxidation was catastrophic in spots with just spikes in others. There is a large coating diffusion zone, and carbides are disintegrating throughout the sample. Plate-like phase forming throughout the sample also. See Fig. 9a.

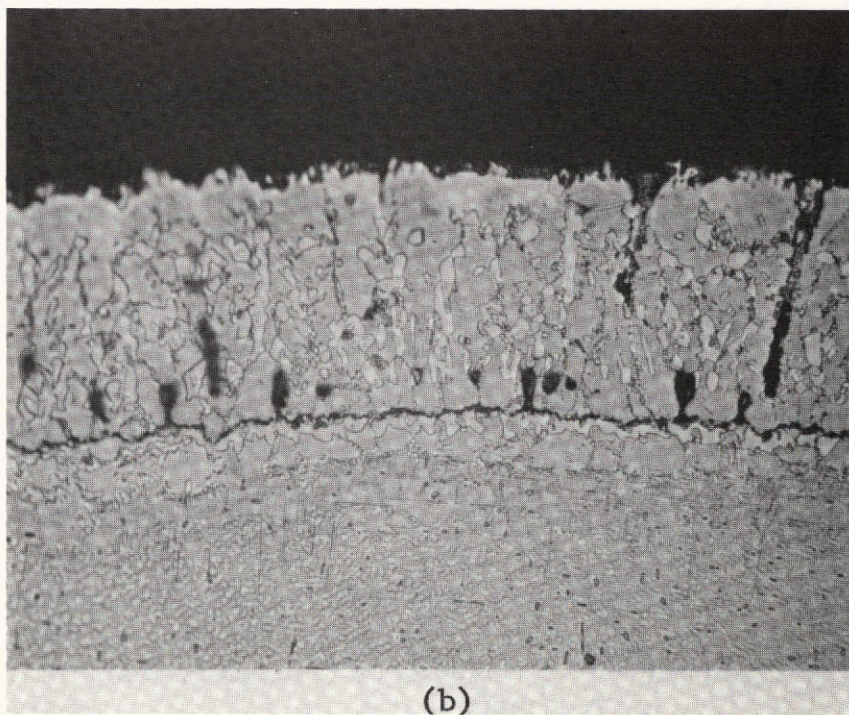
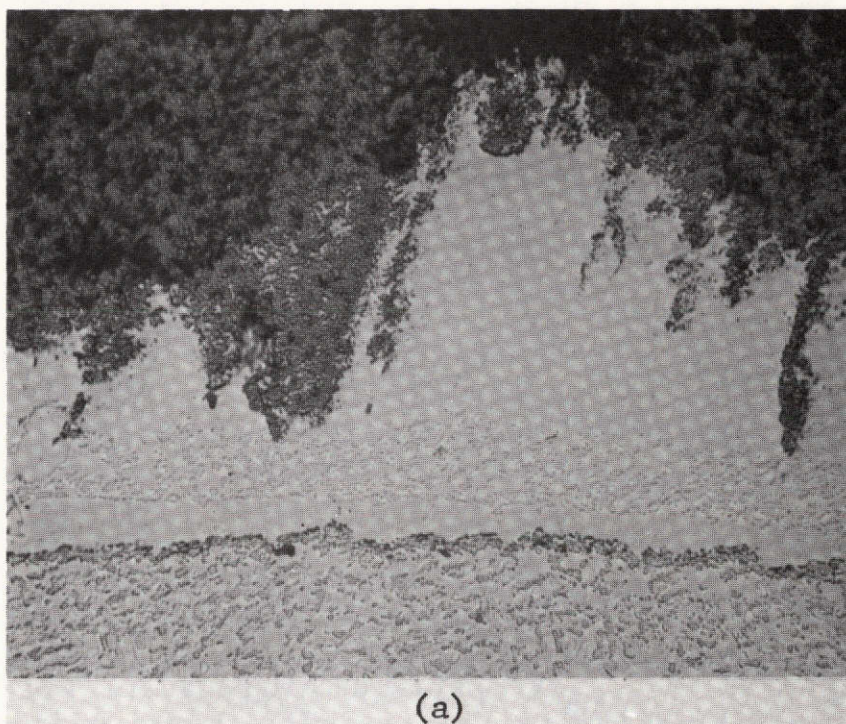


Figure 9 Coatings on NiTaC-13 after 100 hr cyclic furnace oxidation at 1600°F. (a) Fe-25Cr-10Al-1Y. (b) Ni-25Cr-10Al-1Y. 500X

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Composition
Ni-25Cr-10Al-1Y

Comments
Porosity in coating near interface. Very little oxidation. A great deal of decarburization and some plate-phase formation. This can be seen in Fig. 9b.

Ni-30Cr-5Al-1Y

Large carbide denuded zone in substrate. Very little oxidation confined to outer regions of coating. Very faint traces of plate-phase formation.

Ni-35Cr + Al

Large carbide denuded region. Three-layered coating with various phases in each. Oxidation confined to outer regions. Some diffusion of coating material into substrate with subsequent interaction. Plate-phase formation. Some porosity in coating.

Ni-20Cr-15Al-1Y

Very little decarburization. Coating is oxidizing radially. Large oxide layer seen in longitudinal view. Plates associated with carbides. Macro indicates the coating was on the brink of failure.

Co-25Cr-10Al-1Y

Coating intact. Slight decarburization. Oxidation into approximately 1/3 of coating. Substrate interaction is great. Plate phase is formed in interaction zone.

Cyclic Furnace Oxidation: 265 hours, 1093°C

Composition
Fe-30Cr-5Al-1Y

Comments
Coating oxidation extremely severe. Oxidation along coating-substrate interface with many spikes extending into base. Very large interaction zone and many plates. Carbides beginning to disintegrate throughout sample. See Fig. 10.

Fe-25Cr-10Al-1Y

Many internal oxidation pockets in coating. Large diffusion of coating into substrate. Carbides non-existent. Many plates throughout sample.



Figure 10 Fe-30Cr-5Al-1Y on NiTaC-13 after 265 hr
cyclic furnace oxidation at 1093°C. 500X

Composition
Ni-25Cr-10Al-1Y

Comments

Relatively thick oxide scale adhering to a two-phase coating. Internal oxidation of Cr-rich phase. Cr-rich phase growing at the interface and oxide associated with it. Some oxidation spikes into substrate. Carbides disintegrating everywhere else.

Ni-30Cr-5Al-1Y

Fair sized adhering oxide. Internal oxidation of coating very bad. Oxide forming at interface with spikes extruding deep into base material. Carbides disintegrating everywhere else.

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Composition
Ni-35Cr + Al

Comments

Complete diffusion of Al in NiCr. Large precipitates in coating. Oxidation small but surface rough. Large scale decarburization. Fibers disintegrating throughout the sample. Plate phase is coarsening.

Ni-20Cr-15Al-1Y

Thick adhering oxide. Internal oxidation of coating becoming severe. Plates are growing near interface and apparent preferential oxidation down these plates. Carbides breaking up throughout the sample.

Co-25Cr-10Al-1Y

Slight radial oxidation down Cr-rich phase. Coating standing up well. Cr-rich phase precipitating in substrate. Large interaction zone with plates growing ahead of it. Carbides disintegrating throughout sample.

Fe-30Cr-5Al-1Y

Coating oxidized severely and spalled. Further testing of this coating was terminated soon after the 265-hour exposure previously reported.

Fe-25Cr-10Al-1Y

Coating has oxidized and spalled from the sample. Subsequent oxidation of base material is catastrophic. Extensive Fe diffusion into substrate has resulted in the formation of several new phases. Plate phase is throughout the sample, but plates are shorter in zone of pronounced Fe diffusion. Where coating persists, carbide fibers have broken up and most of γ' has been solutioned, leaving only the platelet phase and the γ matrix. See Fig. 11a.

Ni-30Cr-5Al-1Y

Attack is severe. Oxidation is pronounced at the coating-substrate interface, and substrate oxidation is occurring preferentially. Spike oxidation of the plate phase goes deep into substrate. Plate formation and carbide fiber breakup occurs throughout. Decarburization is about 300 μm deep. See Fig. 11b.

Composition

Ni-25Cr-10Al-1Y

Comments

Oxidation is less severe than Ni-30-5-1. However, coating-substrate interface is oxidized. This may be due to length of the pin, with oxidation occurring from the uncoated pin end. Coating is largely unoxidized. Spike oxidation of the plate phase extends into substrate. Plate formation and carbide-fiber breakup occur throughout. Decarburization is about 300 μm deep. See Fig. 11c.

Ni-20Cr-15Al-1Y

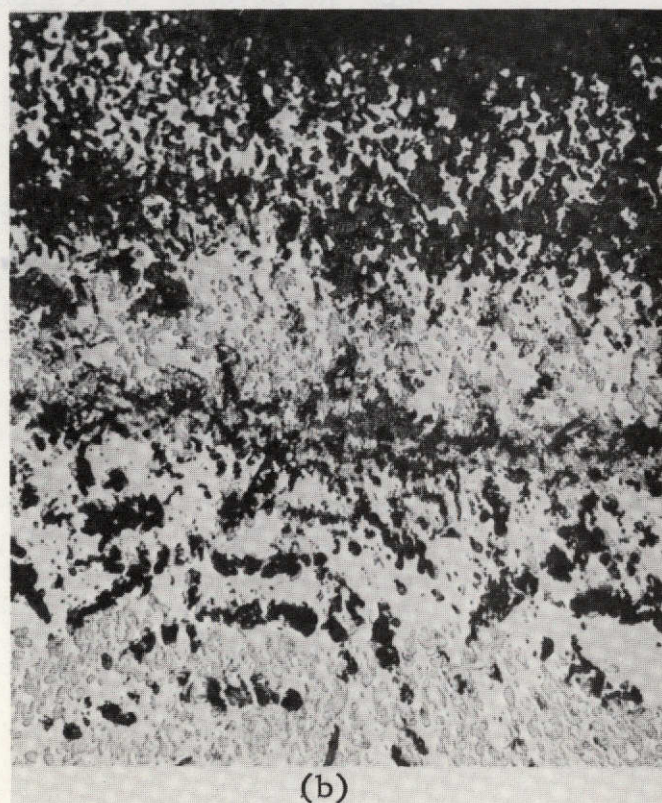
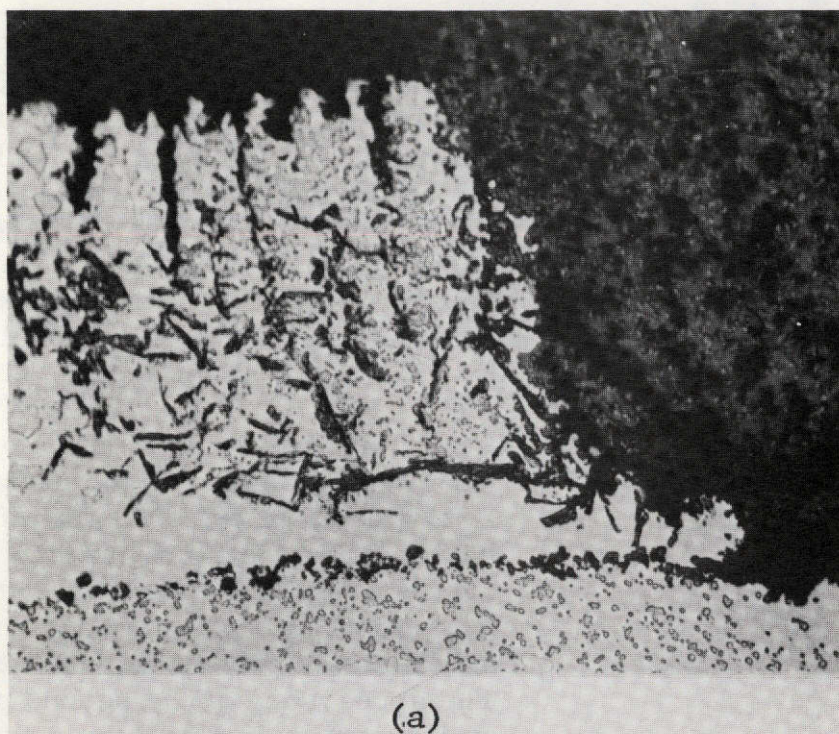
Less spike oxidation than the other two NiCrAlY coatings. Also, decarburization is to a depth of only 100 μm . Plate formation and carbide fiber breakup occur throughout. One pin exhibited excellent substrate protection, while the second showed non-adherence of the coating and heavy oxidation. The appearance of the second pin suggests an interaction between the supporting cement and the pin may be responsible for non-adherence. See Fig. 11d.

Ni-35Cr + Al

Some breakthrough of the coating and oxidation of the substrate, but where coating is continuous, the substrate is well protected. A concentration of Cr-rich precipitates in coating and substrate in the region of the interface may be responsible. Spike oxidation of plate phase near interface. Plate formation and carbide fiber breakup occur throughout. Decarburization occurs to a depth of about 400 μm . See Fig. 11e.

Co-25Cr-10Al-1Y

No coating left on samples; this may be due to coating spalling. Thick adherent oxide extends well into pins. Plate formation and carbide fiber breakup occur throughout. See Fig. 11f.



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Figure 11 Coatings on NiTaC-13 after 500-hr cyclic furnace oxidation test at 1093°C. (a) Fe-25Cr-10Al-1Y. (b) Ni-30Cr-5Al-1Y. 500X

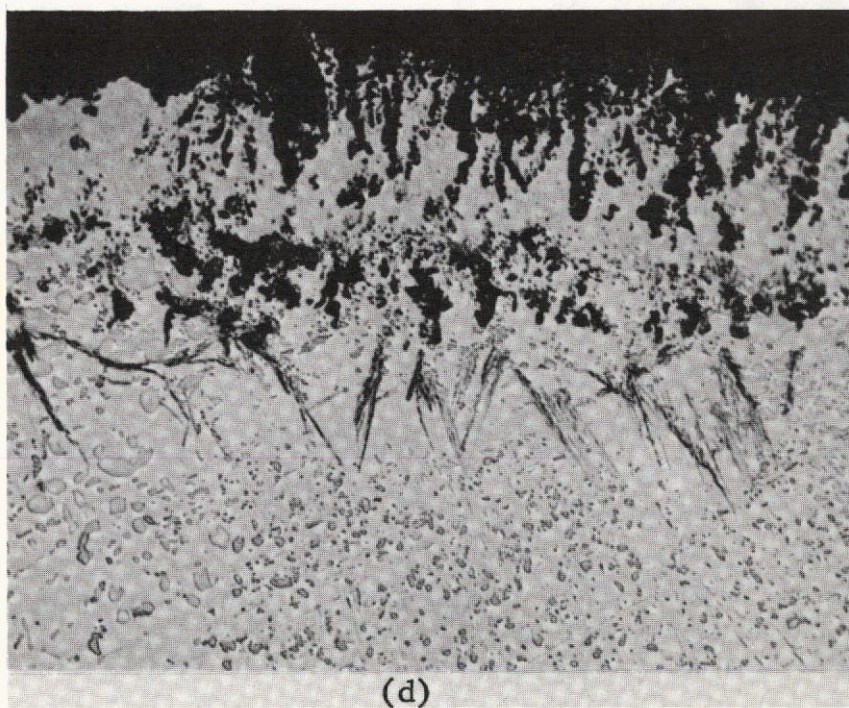
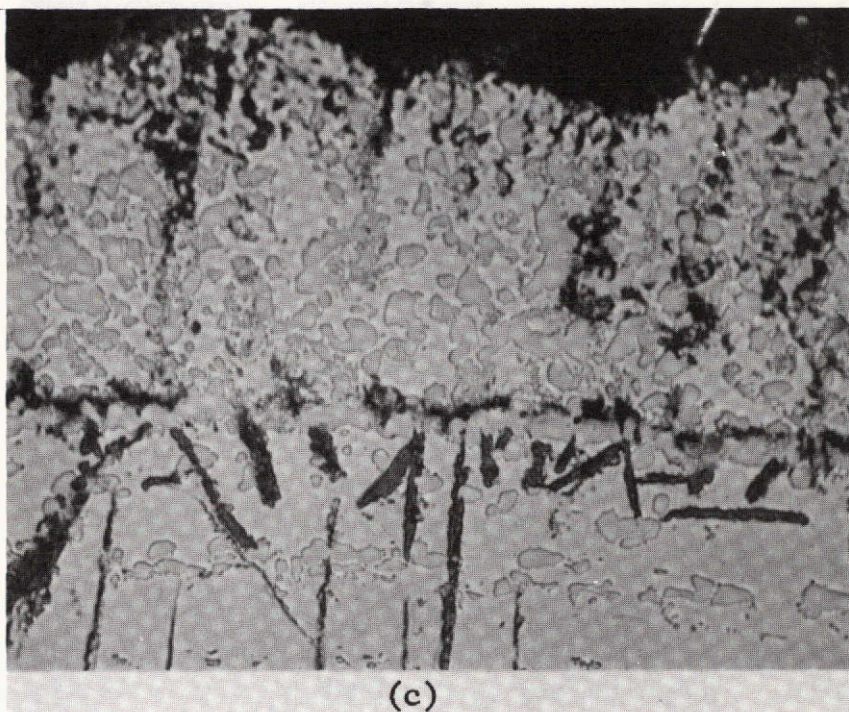
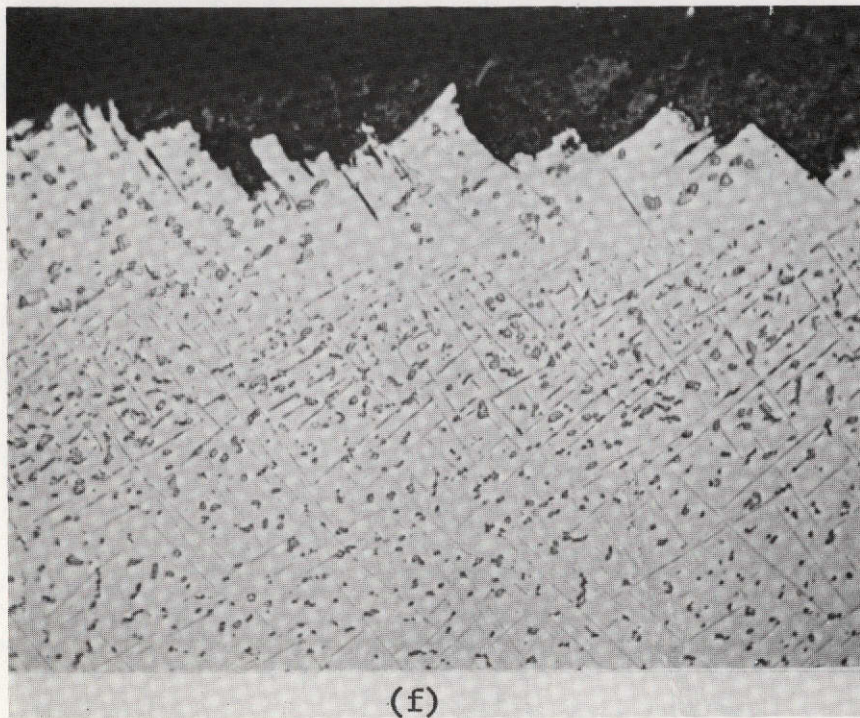
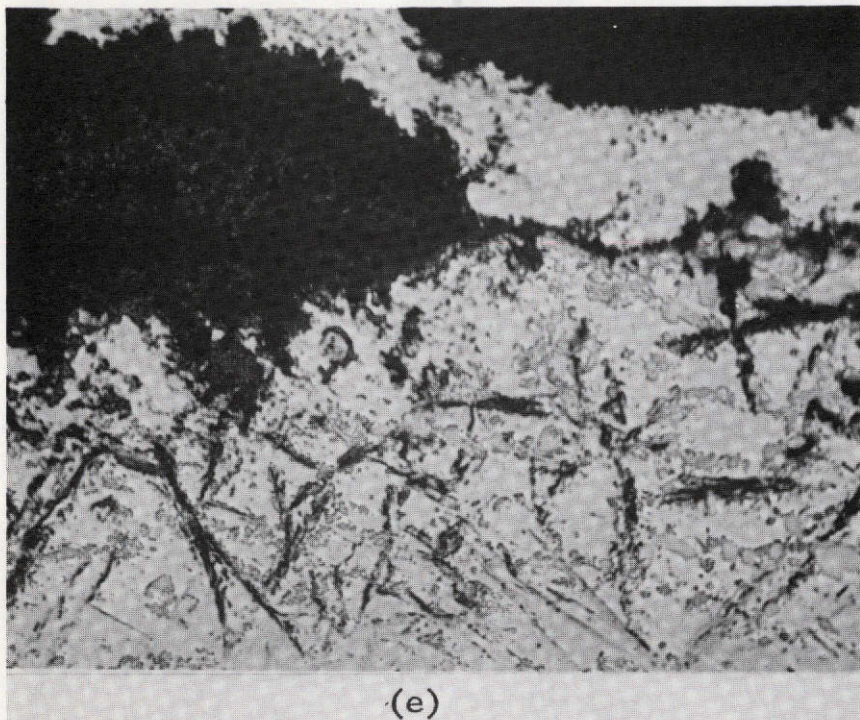


Figure 11 Coatings on NiTaC-13 after 500-hr cyclic furnace oxidation test at 1093°C. (c) Ni-25Cr-10Al-1Y. (d) Ni-20Cr-15Al-1Y. 500X

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Figure 11 Coatings on NiTaC-13 after 500-hr cyclic furnace oxidation test at 1093°C. (e) Ni-35Cr + Al. (f) Co-25Cr-10Al-1Y. 500X

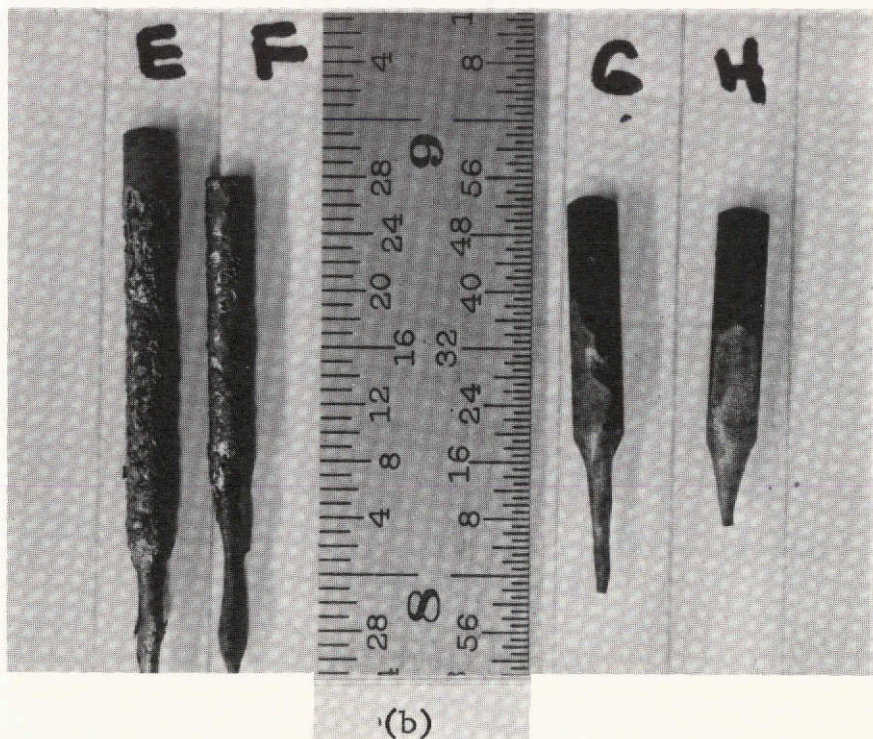
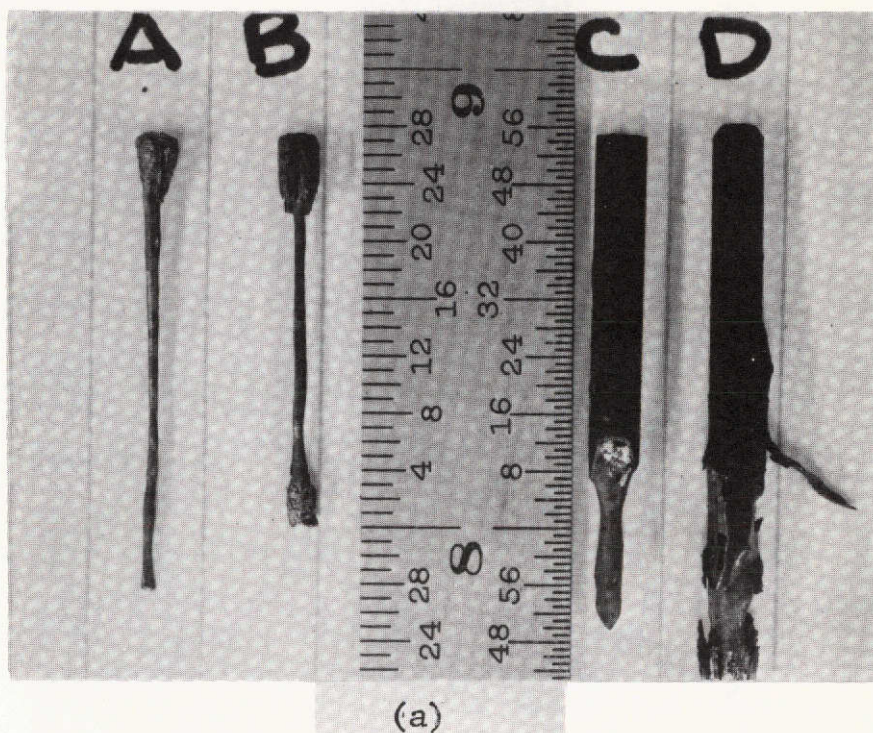


Figure 12 Coated pins after cyclic furnace oxidation 93° to 1093°C, 500 hours.
 (a) Samples A&B; Fe-30Cr-5Al-1Y (265+ hrs). Samples C&D; Ni-25Cr-10Al-1Y.
 (b) Samples E&F; Fe-25Cr-10Al-1Y. Samples G&H; Ni-30Cr-5Al-1Y. ~2.5X

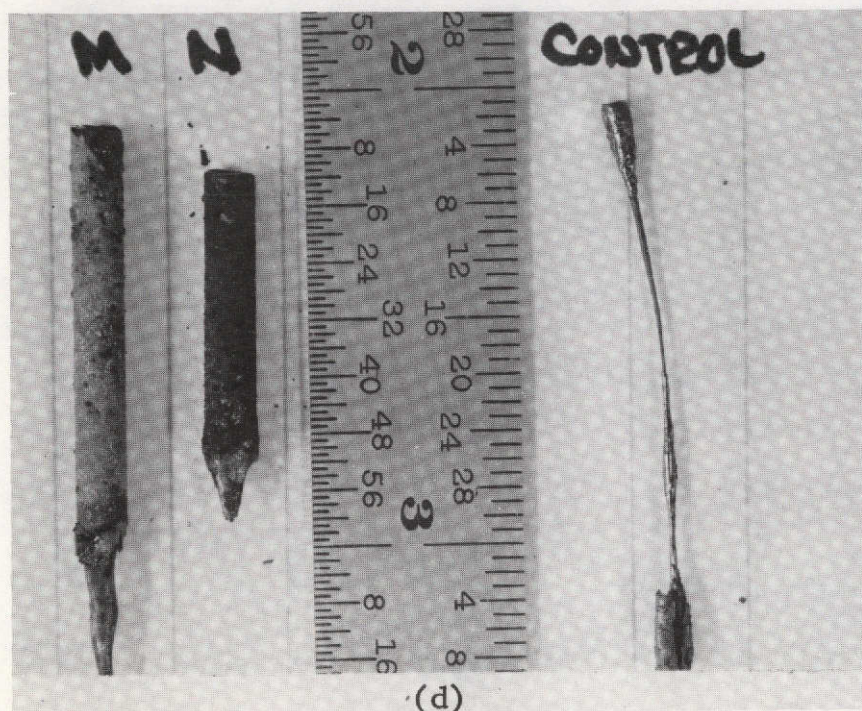
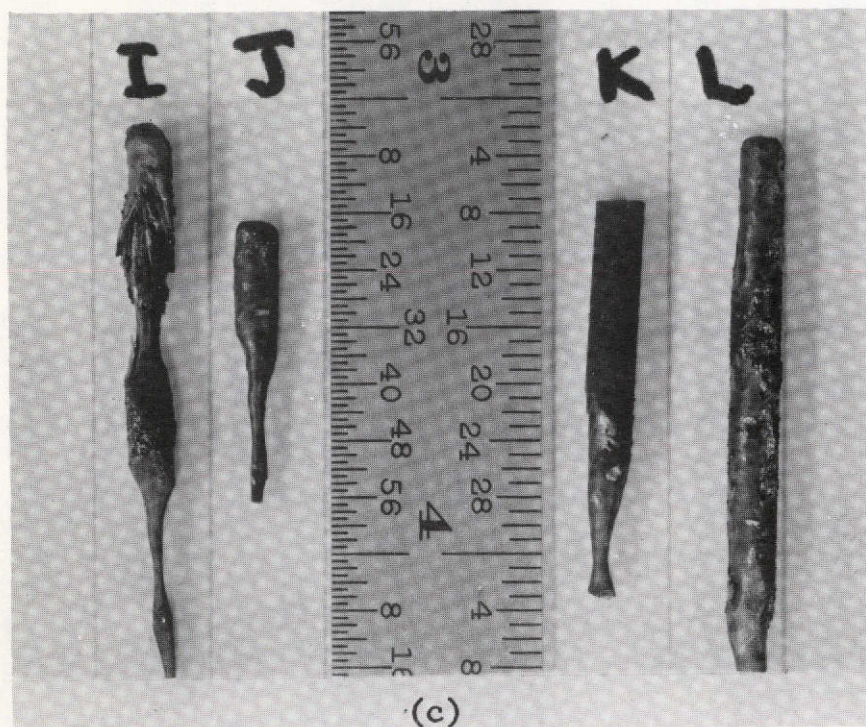


Figure 12 Coated pins after cyclic furnace oxidation 93° to 1093°C for 500 hrs.

(c) Samples I&J; Co-25Cr-10Al-1Y. Samples K&L; Ni-20Cr-15Al-1Y.

(d) Samples M&N; Ni-35Cr + Al. Uncoated control sample (265 hrs). ~2.5X

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Macrographs of the coated pins after cyclic furnace oxidation at 1093°C are shown in Figs. 12a-12d. The uncoated pin cycled for control also is shown.

Metallographic examination of cyclic oxidation tests conducted at 871°C and at 1093°C lead to the recommendation that the coating systems for Task II be Ni-20Cr-15Al-1Y and Ni-35Cr plus Al. The FeCrAlY coatings exhibited severe oxidation and spalling, and resulted in substantial alteration of the phases present in the substrate. The CoCrAlY coating looked promising through the 265-hour exposure at 1093°C. However, the coating could not withstand the 500-hour exposure. The oxidation behavior of this material indicates that coating development using this composition as a starting point should be pursued in the future.

The four Ni-base coatings withstood the 1093°C cyclic exposure well in spite of the severity of the test. Selection of two coatings for Task II could not be made on the basis of macroscopic examination since the coatings all appeared to be protective. Macroscopic examination showed Ni-30Cr-5Al-1Y to have the least oxidation resistance of the four coatings, and that coating was eliminated. The duplex Ni-35Cr + Al had the best oxidation resistance of the coatings and was chosen for this reason. The choice between the remaining two coatings was more difficult. One pin of the Ni-20Cr-15Al-1Y coating showed extremely good protection, while the second pin had little coating retention. However, the decarburization noted on the protected pin was least of all coatings in the program. The other three Ni-base coatings exhibited about 3-4 times as deep decarburization. Why one pin did not retain its coating is unknown, but it may have been due to interaction with the supporting cement. Since the protection from oxidation of one pin was nearly equivalent to that of the duplex coating, and since decarburization was at a minimum, this coating was also recommended for Task II.

B. Cyclic Burner Rig Test

1. Macroscopic Appearance and Weight Change

The first part of Task II was to coat oxidation test pins of NiTaC-13 with Ni-20Cr-15Al-1Y and with duplex Ni-35Cr + Al under the preferred conditions and heat treat them in argon for 3 hours at 1160°C. These pins were cyclically oxidized in a burner rig at AEBG, Lynn, Mass. Based on evaluation of the coating behavior, the cyclic exposure time would be selected for coated test bars.

The burner rig used in this study is located at the General Electric Plant (AEBG) in Lynn, Mass., and is shown in Fig. 13. Jet engine fuel (JP-5) is combusted in the front section of the furnace, and the hot gases impinge at a low velocity (MACH 0.05) on the pins supported on a rotating sample holder

located at the rear of the furnace. The combusted fuel heats the pins to approximately 1093°C. The rear section of the furnace is split and hinged to rotate away, opening to the sample holder. Samples are removed about once an hour and placed in a cooling rack until they cool to below 93°C. The samples are then returned to the burner rig. This process is repeated 6-8 times during normal working hours, and the samples remain at 1093°C for 16 hours overnight. Once each day, pin samples were cooled to room temperature and weighed, visually examined and photographed.

The appearance of coated and uncoated cyclic burner rig exposure pins after different exposure times is shown in Fig. 14. Sheets of an unprotective oxide form and spall on the uncoated NiTaC-13, while the coated pins show near-zero spalling of the light oxide that forms. The uncoated pins were all removed by approximately 200 hours of cycling, while the last of four duplex coated pins was considered failed on visual examination at approximately 630 hours. Some pin-cement interaction can be seen in photographs of the duplex sample. The final Ni-20Cr-15Al-1Y coated pin was removed at 830 hours. The pin could have continued longer, except for localized attack in one area and extensive oxidation at both ends of the pin.⁽⁷⁾ This pin is the NiCrAlY coated pin shown in Fig. 14 to 535 hours and in Fig. 15 to 830 hours.

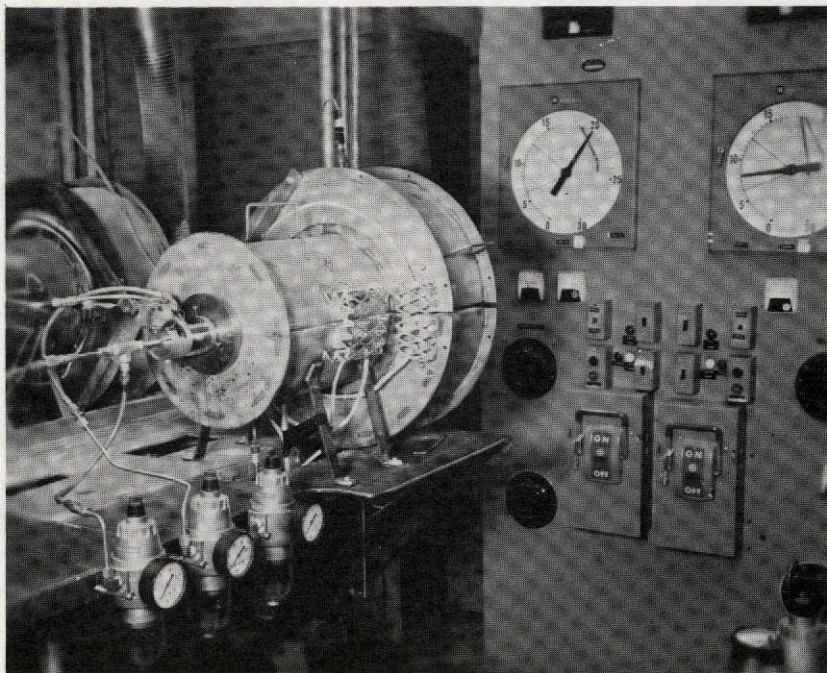


Figure 13 Photograph of one of the burner rigs used at AEBG, Lynn, Mass. Larger diameter rear of furnace is hinged so it may be pivoted away to remove samples. Temperature in this section of the rig is approximately 1093°C. In cyclic oxidation testing, samples were removed about once an hour, cooled below 93°C, and returned to the furnace. Each day this process was repeated for 8 hours and then the samples were isothermally exposed to 1093°C for 16 hours.

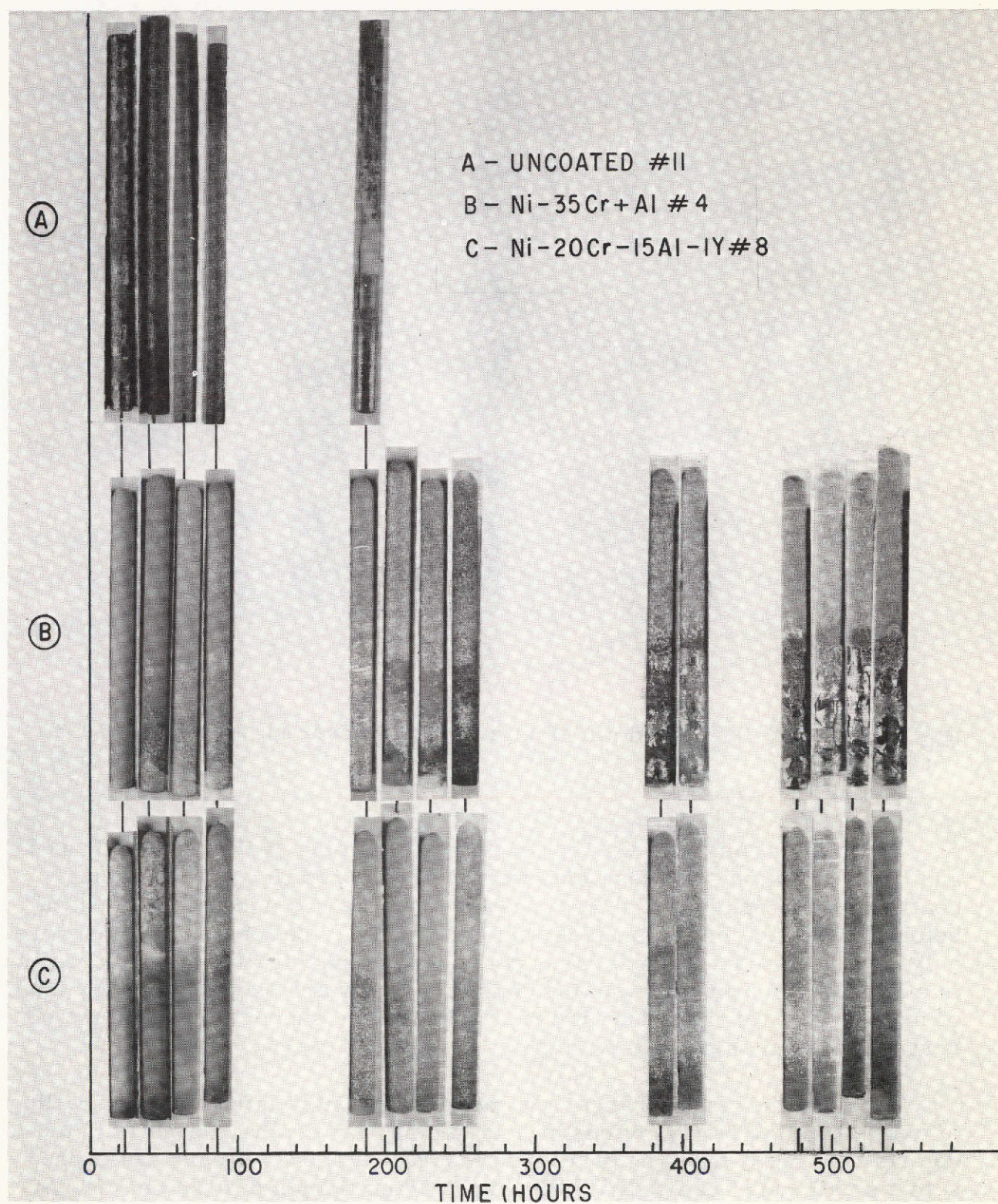


Figure 14 Appearance of uncoated and coated NiTaC-13 burner rig oxidation pins as a function of cyclic burner rig exposure time (93° to 1093°C). 1.6X

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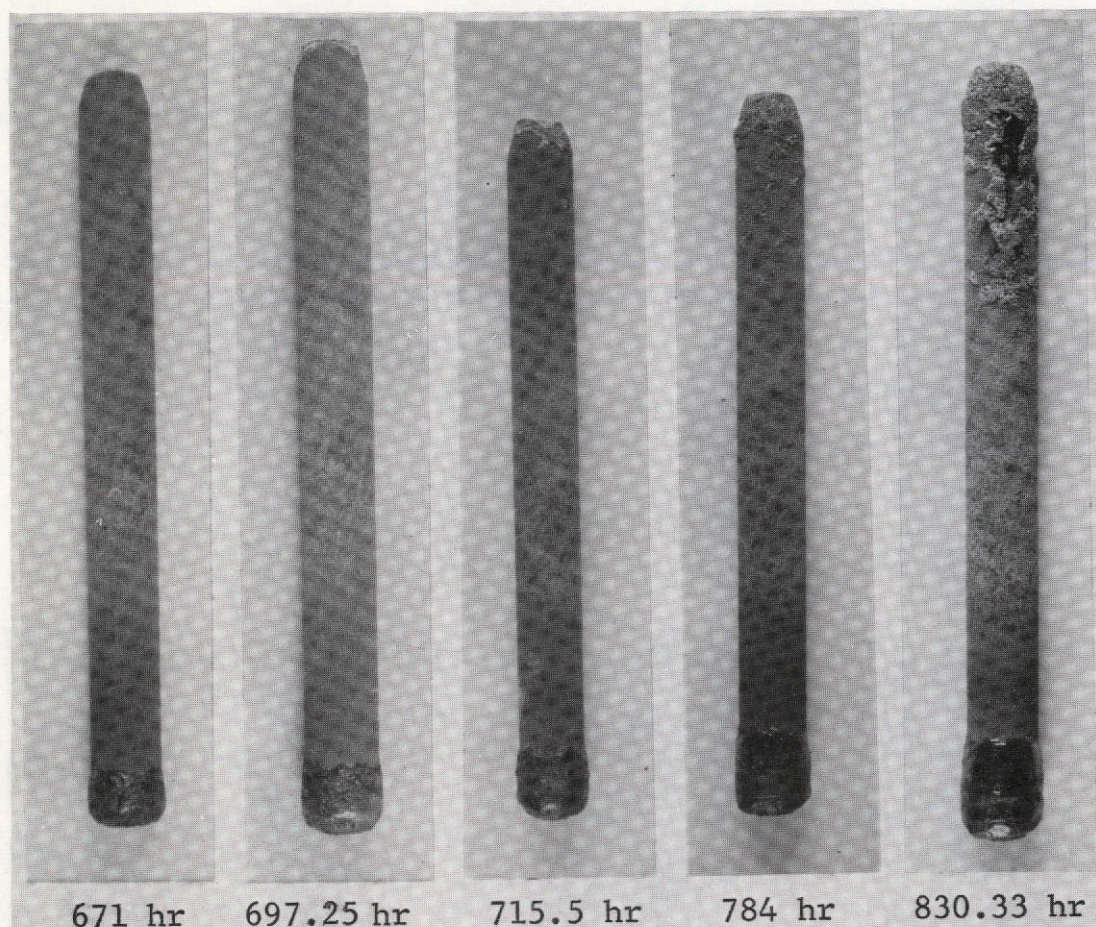


Figure 15 NiCrAlY coated pin #8 after cyclic burner rig exposure (93° to 1093°C).
3X to 3.5X

Oxidation at pin ends was common to all the pins cycled in both Task I and II. The bottoms of these pins were held in a rotating fixture during coating deposition. Even though the segment that was uncoated was cut off before exposure, the cut surface was bare. Also, the tops of the pins were only lightly coated. This is due to the fact that, physically, vapor deposition is a line-of-sight process and the ends of the pins are exposed to a low angle of incidence of vapor. Also, interactions with the support cement were observed, as seen on sample #4 in Fig. 14.

Because the weight change data might be strongly influenced by spalling of oxide from the bare portions of coated pins, studies have been initiated to determine a more meaningful test procedure. A NiTaC-13 pin was capped with a small weld bead of Ni-20Cr, and 1.27 cm length of 0.23 cm dia. Ni-20Cr was butt welded to the other end. The length of Ni-20Cr wire became the pin end inserted in the sample holder during normal evaporation of a Ni-20Cr-15Al-1Y coating. A portion of that end was coated, and all of the weld bead cap was coated. After heat treatment, the bottom of the pin was cut off, at

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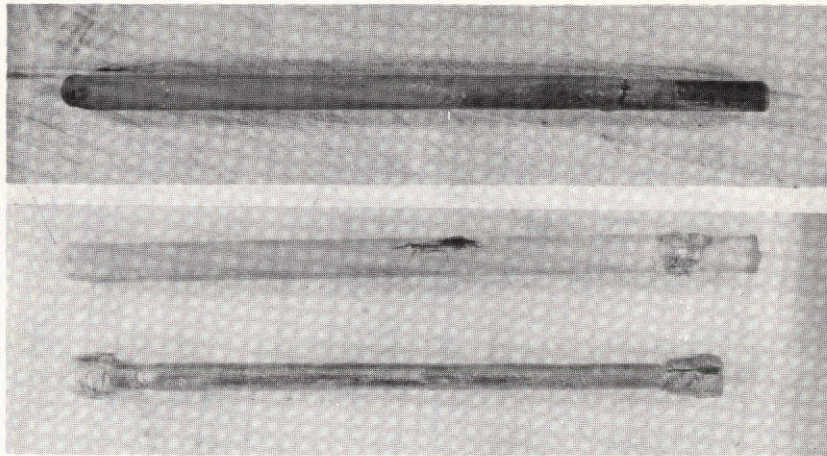


Figure 16 2X macrographs of pins (93° to 1093°C) for the cyclic furnace oxidation test. The top is an uncycled NiCrAlY coated pin. Before coating, the left end was capped with a weld bead of Ni-20Cr and the right end was welded to a short rod of Ni-20Cr. After the pin assembly was coated, the uncoated section of the Ni-20Cr rod that was in the coating holder was removed. The middle macrograph is the same pin after 451 one hour long oxidation cycles. The crack noted at the center of the sample developed between 323 and 348 hours. The bottom pin is uncoated NiTaC-13 cyclically oxidized for 163 hours.

approximately the position between coated and uncoated Ni-20Cr. This pin then consisted of a normally coated midsection of NiTaC-13 with coated Ni-20Cr segments at each end and an uncoated Ni-20Cr bottom. The pin is shown in Fig. 16, as coated and after 451 cycles (451 hours) in the cyclic furnace oxidation test. A longitudinal crack is shown which developed between 323 and 348 hours. The crack enlarged in the next 100 hours of furnace cycling, but little spalling occurred. An uncoated NiTaC-13 pin furnace cycled simultaneously is shown in the figure as well. It was removed at 163 hours.

The weight change data is plotted in Fig. 17. Data for bare pins are compared in Fig. 17a for the cyclic furnace and cyclic burner rig tests. The curves are essentially identical for the first 100 hours. During this time, the burner rig samples were being cycled 6-8 times a day. For the next several days, the burner rig pin was held at 1093°C with no cycling. Apparently, oxidation continued at a rapid rate, but spalling nearly ceased with the net result that little weight change occurred. When cycling began again, the thickened oxide layer that had formed spalled and the weight change data returned to near the level of the cyclic furnace test.

The severity of the 1093°C burner rig test used in Task II and the 1093°C cyclic furnace oxidation test used in Task I are approximately comparable.

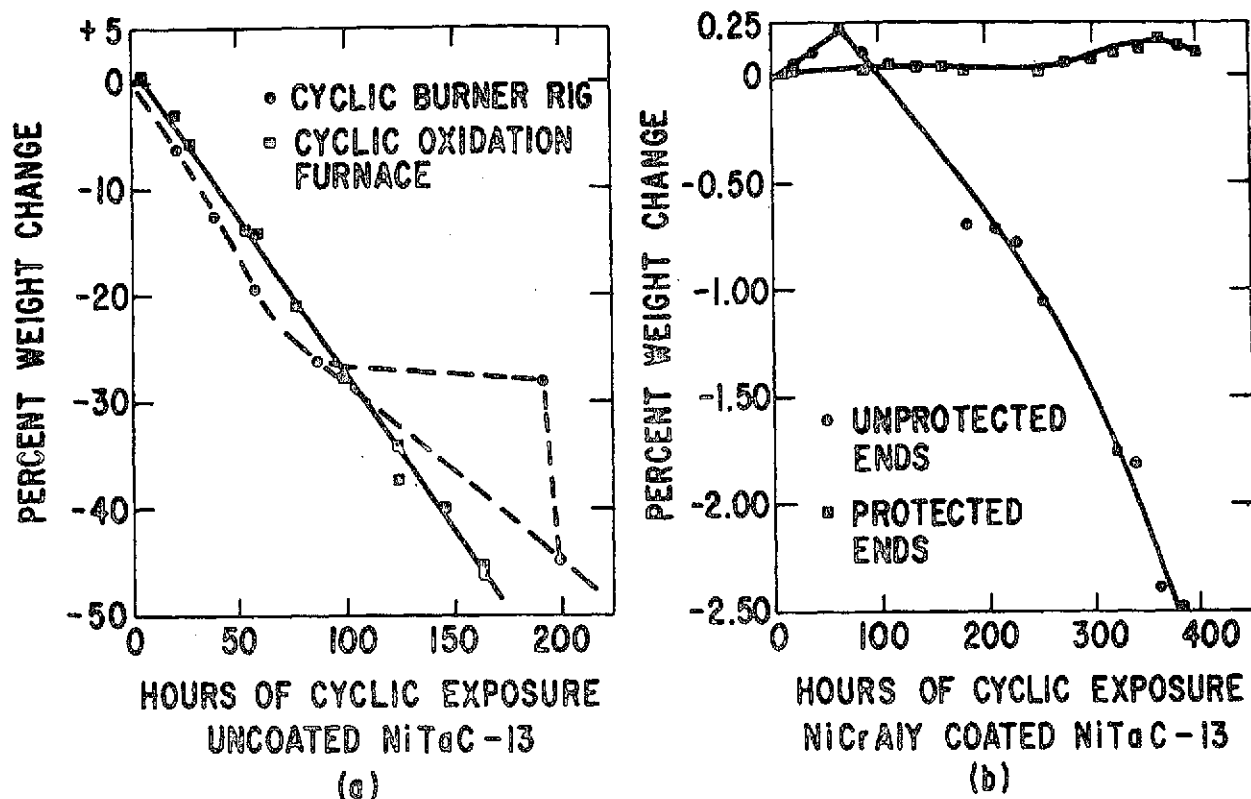


Figure 17 (a) Comparison of weight change as a function of cyclic oxidation exposure time for uncoated NiTaC-13 pins in burner rig or cyclic furnace testing, 93° to 1093°C. From 100 to 200 hours, two lines are shown for the burner rig cycled pin: the upper one shows actual change for the pin held isothermally for most of that period at 1093°C, while the lower one is extrapolated to approximate the results expected if cycling had occurred during that period. (b) Comparison of weight change as a function of cyclic oxidation exposure time for NiCrAlY coated NiTaC-13 for pins with protected or unprotected ends. Pin cycled with protected ends was done in the cyclic furnace oxidation test, while pin with unprotected ends was done in the burner rig. Cycling, 93° to 1093°C.

The dynamic conditions in the burner rig may be more severe than the furnace conditions, but the 6-8 cycles/day in the burner rig are less severe than the 24 cycles/day in the automatically cycled furnace test.

Figure 17b compares weight change results for two Ni-20Cr-15Al-1Y coated pins, one with protected ends cycled in the furnace test and one with unprotected ends cycled in the burner rig, both to 1093°C. Since the two tests give equivalent results for bare pins (Fig. 17a), the more rapid weight loss shown in Fig. 17b for the burner rig test pin can be interpreted as due principally to the unprotected ends. One would expect burner rig exposure of end-protected coated pins to show little or no weight change.

The weight change data are given in Table I for the bare pin and coated pin with protected ends cycled in the furnace oxidation test. Both percent weight change and weight change per unit area are tabulated. Spalling causes tremendous weight loss for uncoated NiTaC-13, but Ni-20Cr-15Al-1Y coated NiTaC-13 undergoes essentially no weight change in 451 hours, even though a coating crack existed for more than 100 hours of furnace cycling.

Figure 18 shows weight change as a function of cycling time in the burner rig for three pins, one uncoated, one duplex coated, and one NiCrAlY coated. Data for all twelve cycled pins are given in Table II. As has been noted, the data for bare pins are true values, while data for coated pins reflect, almost totally, weight change resulting from oxidation of and spalling from the unprotected ends. With this in mind, the data for coated pins can be considered only qualitatively. Two main points can be made. Both coatings are quite protective for NiTaC-13 burner rig cycled to 1093°C, and neither coating stands out as superior to the other, based on weight loss data. However, macroscopic observations⁽⁷⁾ lead to the conclusion that the NiCrAlY coating is superior. The appearance of this coating is more uniform from pin to pin and along each pin. Surfaces of the duplex coated samples are generally more mottled, and there is occasionally evidence of blistering or penetration.

TABLE I
Weight Change Measurements for Coated and Bare NiTaC-13
in Cyclic Furnace Oxidation 93° to 1093°C

Uncoated NiTaC-13 w ₀ = 1.83577 gms.				Ni-20Cr-15Al-1Y Coated NiTaC-13*** w ₀ = 2.09796 gms.			
hrs.	Δw (gms.)	mg/cm ²	%	hrs.	Δw (gms.)	mg/cm ²	%
0	--	--	--	0	--	--	--
6	+ .01143	+ 3.4	+ 0.6	22	.00066	.17	.03
22	-.05430	- 15.9	- 3.0	87	.00035	.09	.02
29	-.10614	- 31.2	- 5.8	110	.00088	.22	.04
53	-.25490	- 74.8	-13.9	137	.00088	.22	.04
59	-.26122	- 76.7	-14.2	160	.00078	.20	.04
77	-.38636	-113.4	-21.0	181	.00049	.12	.02
99	-.51124	-150.1	-27.8	253	.00034	.09	.02
124	-.62447	-183.3	-34.0	277	.00122	.31	.06
124	-.68365	-200.7	-37.2	301	.00173	.44	.08
145	-.73432	-215.5	-40.0	323	.00233	.59	.11
163	-.83495	-245.1	-45.5	*348	.00252	.64	.12
163	-.85191	-250.1	-46.4	**348	-.02121	-5.39	-10.10
				369	.00380	.97	.18
				387	.00294	.75	.14
				401	.00199	.51	.09

*Coating crack developed between 323 and 348 hours.

**Questionable data point, cause unknown.

***Ends protected with Ni-20Cr prior to coating.

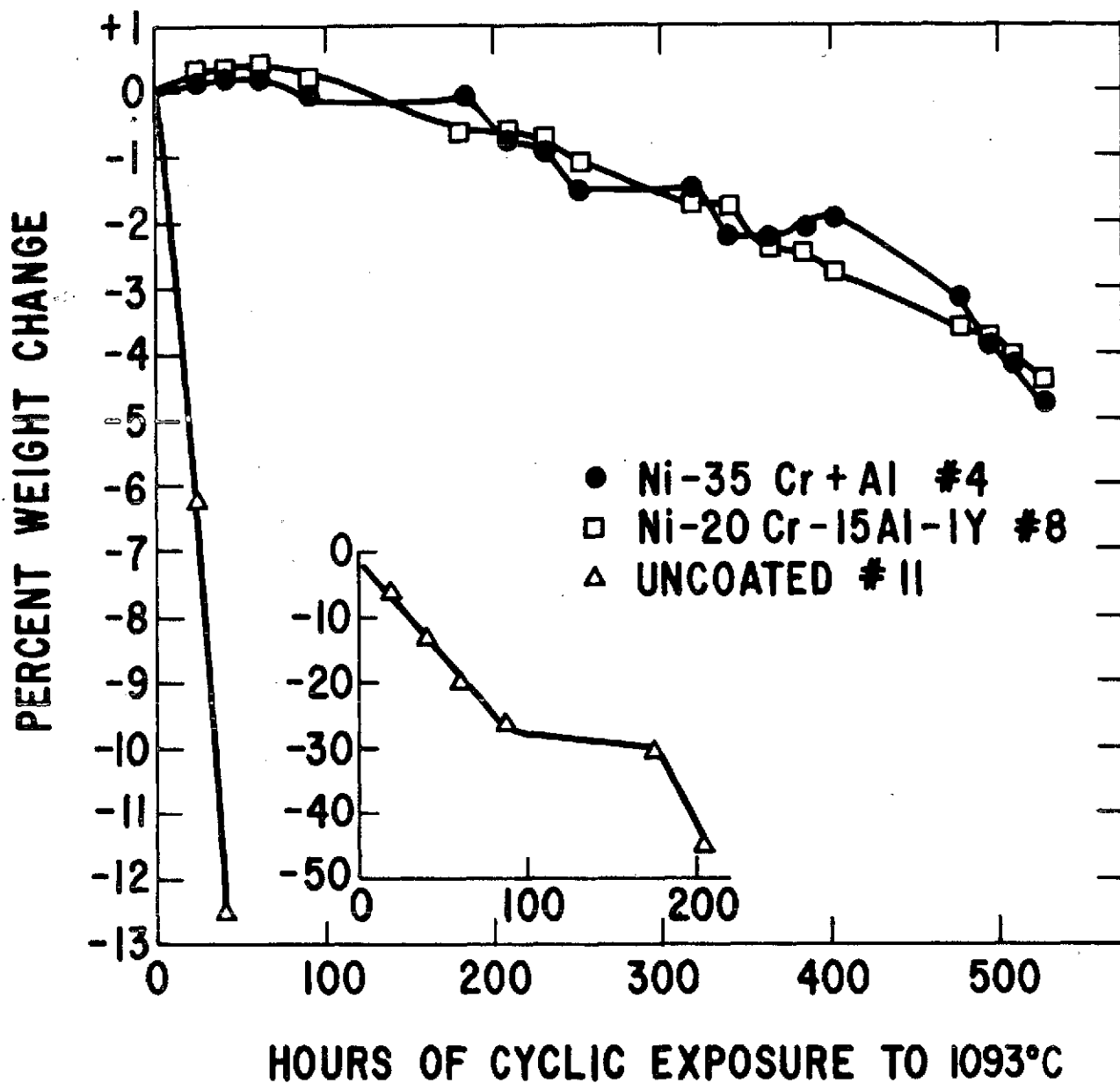


Figure 18 Uncoated and coated NiTaC-13 pins subjected to the 93° to 1093°C cyclic burner rig test: percent weight change versus cyclic oxidation exposure time.

TABLE II

Weight Change Measurements for Coated and Bare NiTaC-13
in the Cyclic Burner Rig Test, 93° to 1093°C

Ni-35Cr + Al Coated NiTaC-13*

Time Hrs./Min.	Cycles	#1 w _O = 1.6244		#2 w _O = 1.6630		#3 w _O = 1.5842		#4 w _O = 1.5480	
		wt. (gms.)	%	wt. (gms.)	%	wt. (gms.)	%	wt. (gms.)	%
22/50	6	1.6283	.24	1.6648	.11	1.5874	.20	1.5486	.04
40/30	9	1.6285	.25	1.6654	.14	1.5890	.30	1.5490	.06
64/--	16	1.6270	.16	1.6671	.25	1.5917	.47	1.5495	.10
87/35	23	1.6233	-.07	1.6668	.23	1.5920	.49	1.5475	-.03
184/35	32	1.6242	-.01	1.6573	-.34	1.5937	.60	1.5363	-.05
208/45	40	1.6233	-.06	1.6607	-.14	1.5963	.76	1.5354	-.81
229/25	44	1.6230	-.09	1.6618	-.07	1.5965	.78	1.5346	-.87
252/25	51	1.6214	-.18	1.6624	-.04	1.5969	.80	1.5241	-1.54
319/55	54	1.6021	-1.37	at 250 hrs.		1.5983	.89	1.5242	-1.54
341/20	60	1.5998	-1.51			1.6003	1.02	1.5145	-2.16
363/20	67	at 341/50				1.6002	1.01	1.5143	-2.18
384/--	74					1.6003	1.02	1.5159	-2.07
406/40	79					1.6003	1.02	1.5179	-1.94
479/15	86					at 414/20		1.5000	-3.10
493/50	93							1.4878	-3.89
513/30	98							1.4839	
535/50	106							1.4750	
558/20	113							1.4798	
631/15	119							1.4801	
652/15	128							at 628/15	

TABLE II (Cont'd.)

Ni-20Cr-15Al-1Y Coated NiTaC-13*

Time Hrs./Min.	Cycles	#5 $w_o = 1.6244$		#6 $w_o = 1.3831$		#7 $w_o = 1.4351$		#8 $w_o = 1.3887$	
		wt. (gms.)	%	wt. (gms.)	%	wt. (gms.)	%	wt. (gms.)	%
22/50	6	1.5423	.06	1.3838	.05	1.4367	.11	1.3895	.06
40/30	9	1.5428	.09	1.3853	.16	1.4370	.13	1.3902	.11
64/--	16	1.5432	.12	1.3861	.22	1.4383	.22	1.3918	.22
87/35	23	1.5414	0	1.3848	.12	1.4368	.12	1.3904	.12
184/35	32	1.5396	-.12	1.3741	-.65	1.4348	-.02	1.3788	-.71
208/45	40	1.5294	-.78	1.3741	-.65	1.4341	-.07	1.3785	-.73
229/25	44	1.5281	-.86	1.3739	-.67	1.4331	-.14	1.3778	-.78
252/25	51	1.5270	-.93	1.3725	-.79	1.4313	-.26	1.3739	-1.07
319/55	54	at 250 hrs.		1.3618	-1.07	1.4322	-.20	1.3643	-1.76
341/20	60			1.3592	-1.54	1.4223	-.89	1.3635	-1.81
363/20	67			1.3554	-2.00	1.3759	-4.13	1.3554	-2.40
384/--	74			1.3552	-2.02	1.3695	-4.57	1.3541	-2.49
406/40	79			1.3561	-1.95	1.3497	-5.95	1.3500	-2.79
479/15	86			1.3425	-2.94	at 414/20		1.3387	-3.60
493/50	93			1.3426	-2.93			1.3359	-3.80
513/30	98			1.3425	-2.94			1.3324	-3.80
535/50	106			1.3251	-4.19			1.3265	-4.48
558/20	113			1.3283	-3.96			1.3240	-4.66
631/15	119			1.3295	-3.88	at 558/20			
652/15	128			1.3229	-4.35				
671/--	132			1.3239	-4.28				
697/15	142			1.3246	-4.23				
715/15	146			1.3252	-4.19				
784/55	150			1.3268	-4.07				
830/20	154			1.3242	-3.90				

TABLE II (Cont'd.)

Uncoated NiTaC-13

Hrs./Min.	Cycles	#9 $w_0 = 1.7842$		#10 $w_0 = 1.7813$		#11 $w_0 = 1.7790$		#12 $w_0 = 1.7841$	
		wt. (gms.)	%	wt. (gms.)	%	wt. (gms.)	%	wt. (gms.)	%
22/50	6	1.6192	-9.25	1.6395	-7.96	1.6680	-6.24	1.6805	-5.81
40/30	9	1.5037	-15.72	1.5260	-14.33	1.5574	-12.46	1.6613	-6.88
64/--	16	1.4220	-20.30	1.3720	-22.98	1.4302	-19.61	at 23/50	
87/35	23	at 46/15		1.2001	-32.63	1.3087	-26.44		
184/35	32			at 92/25		1.2790	-28.11		
208/45	40					0.9791	-44.96		
						at 201/55			

*No precautions taken to protect ends.

2. Microscopic Appearance

As was noted in Task I, microstructural changes occur in the substrate during burner rig cycling between approximately 93°C and 1093°C. Figures 19 and 20 show sequential changes with increased cycling times for uncoated NiTaC-13. In Fig. 19 are longitudinal sections with the fiber axis vertical in a-c and horizontal in d. Figure 20(a-d) shows longitudinal sections with the fiber axis horizontal. Figure 20(e) is a transverse section.

Platelets are found in all the photographs in Figures 19 and 20. Very few platelets are seen after 23 hours of burner rig cycling (four are seen in Fig. 19a), and all are quite short. Roughly twice the number of platelets are seen after 47 hours. A dramatic increase in number and size of platelets occurs between 47 and 91 hours. Little change in platelet size or number is apparent at 201 hours. Other changes are occurring in the microstructure. The γ' phase is altered from individual cubic particles as-solidified to a highly agglomerated, nearly continuous phase after 201 hours of cycling. The relative fractions of γ' and γ may also be changing. The fiber phase also begins to show agglomeration and segmenting as cycling proceeds. The bladelike fiber cross-sections of Fig. 1 become angular in cross-section in Fig. 20(e).

The composition of the platelet phase as determined by electron microprobe analysis is given as approximately $\text{Ni}_{53}\text{Co}_{2.5}\text{Cr}_{17}\text{V}_9\text{Ta}_1\text{Re}_6\text{W}_{1.5}\text{Al}_{10}$. No positive identification has been made of the crystallography of the phase because of difficulties in isolating the phase. The platelet precipitates from γ' on $\{111\}$ planes in γ' . Presumably, the close-packed plane of the precipitate is nearly coherent with that of γ' . From Figs. 20c and e, it appears that the platelets are probably square rather than blade-like, since the intercept lengths of platelet and polished surface are similar for both longitudinal and transverse sections. The platelet size seems to be limited by the length of $\{111\}$ in γ' available. The following sequence is a possible explanation. Initial precipitation is within single γ' particles or within the thin γ network. As the platelet precipitates, it grows primarily in γ' , and the composition of the surrounding γ' changes, possibly resulting in a change in lattice parameter. Coarsening of γ' occurs to adjust to the new γ - γ' interfacial energies, and continuity from γ' particle to particle is obtained. The platelet phase is then able to grow in the plane of the precipitate sheet. No significant coarsening of the platelet is observed, only extension, which maximizes the low energy γ' -platelet coherent interfaces.

No gradient in numbers of platelets from exposed surface inward is noted for 91 hours or more of cyclic exposure. Some gradient may exist for shorter exposures, with more particles near the surface. It was thought that diffusion of oxygen into the alloy may have had an effect on precipitation. Samples were quartz encapsulated at a vacuum of 10^{-7} torr and cycled as encapsulated in a furnace. Platelets were observed in approximately the same density as for burner rig exposed samples after vacuum cycling for 25 to 150 hours.

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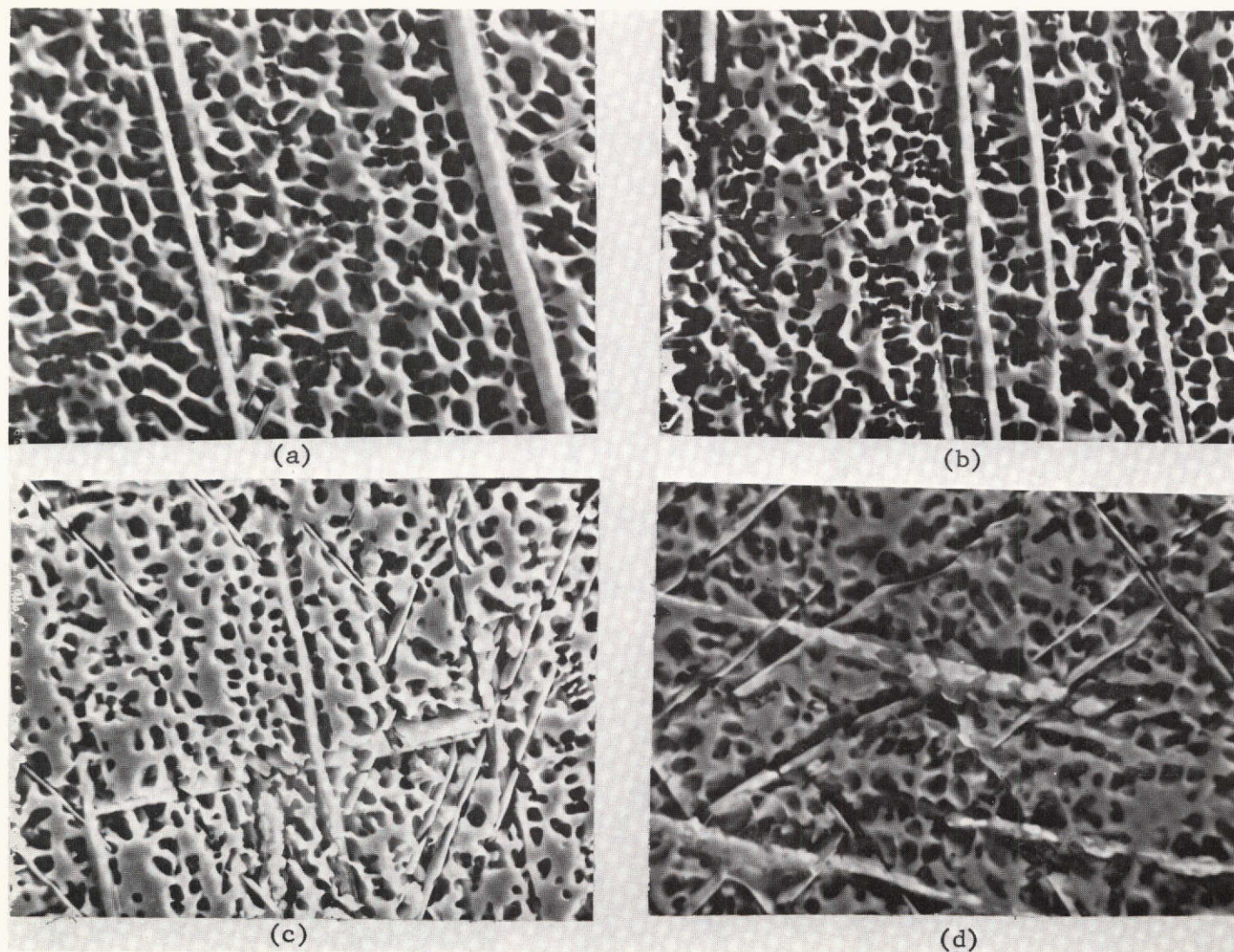


Figure 19 Scanning electron micrographs of uncoated NiTaC-13 pins exposed to the cyclic burner rig test (93° to 1093°C); longitudinal section at 2000X.
(a) 23 hrs; (b) 47 hrs; (c) 91 hrs; and (d) 201 hrs.

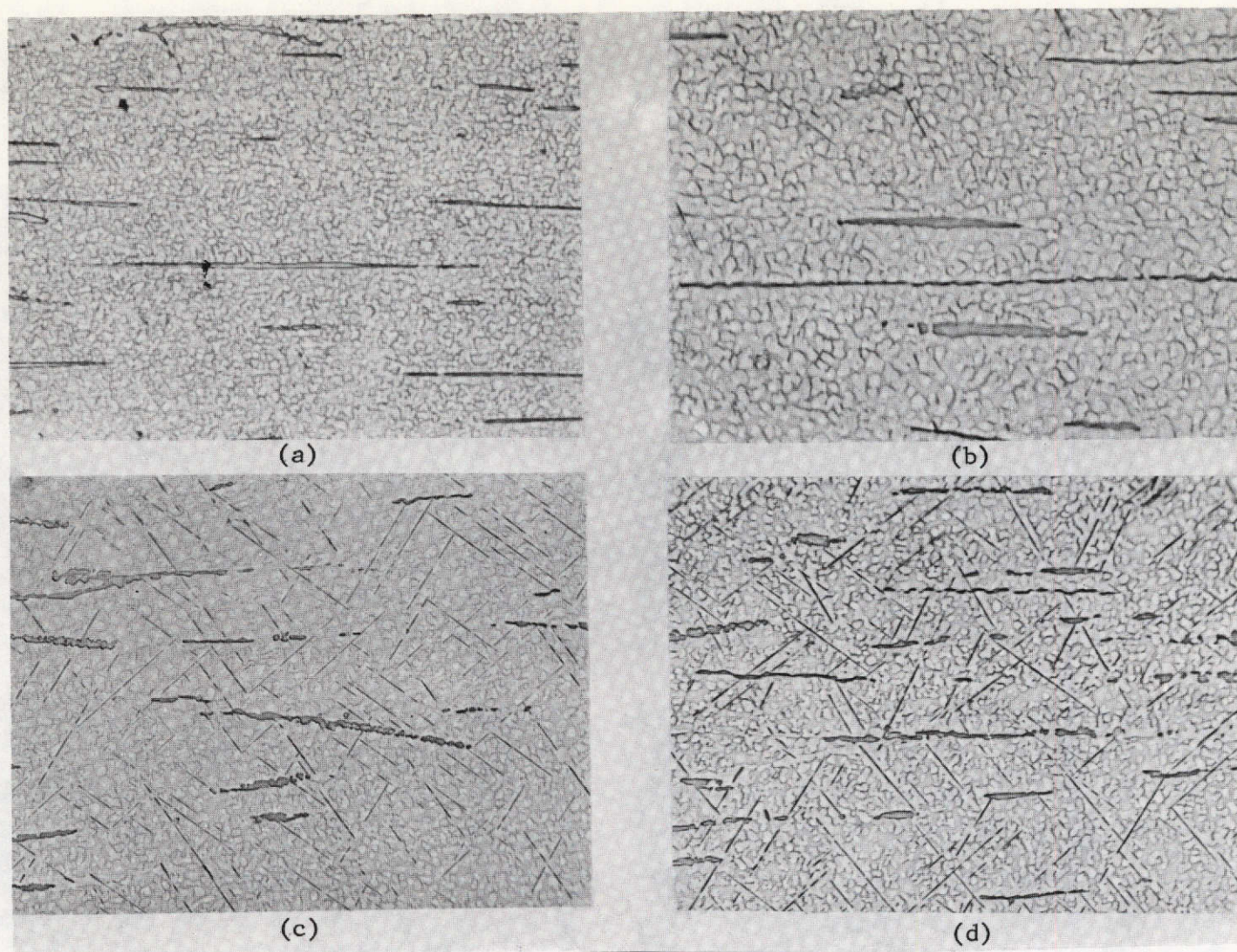


Figure 20 Uncoated NiTaC-13 pins exposed to the cyclic burner rig test 93° to 1093°C; longitudinal. (a) 23 hrs (440X); (b) 47 hrs (1100X); (c) 91 hrs (704X); and (d) 200 hrs (704X).



Figure 20 (continued): (e) Uncoated NiTaC-13 cyclically oxidized in the burner rig for 91 hrs, 93° to 1093°C. Transverse section, 704X.

Microstructures of longitudinal sections of burner rig cycled coated samples are shown in Figs. 21 and 22. The fiber axis is horizontal. For NiCrAlY coated pins, the microstructure of the substrate changes with increased burner rig cycling time. The platelet phase does coarsen somewhat, and the zone denuded of fibers moves further into the substrate. However, little change occurs in the coating. The regions show that the coating thickness is retained through 830 hours exposure, although oxidation within the coating seems more severe than for shorter exposures. All four sections show the coarse, dark phase that appears to follow the platelets from the original coating-substrate interface into the substrate. The bright particles are Cr-rich, probably b. c. c. α Cr, while the bulk of the coating is Ni and Al.

A similar sequence for duplex coated samples (Fig. 22) shows much more of the dark phase parallel to the platelets and more internal oxidation of the coating in less exposure time. The outer layer in the 250 hour sample is rich in Ni and Al, the next layer is Cr-rich, the third layer is Ni- and Al-rich, and the fourth layer is Cr-rich. At longer cycle times, these layers seem to be less continuous and the coating more homogeneous, indicative of substantial interdiffusion.



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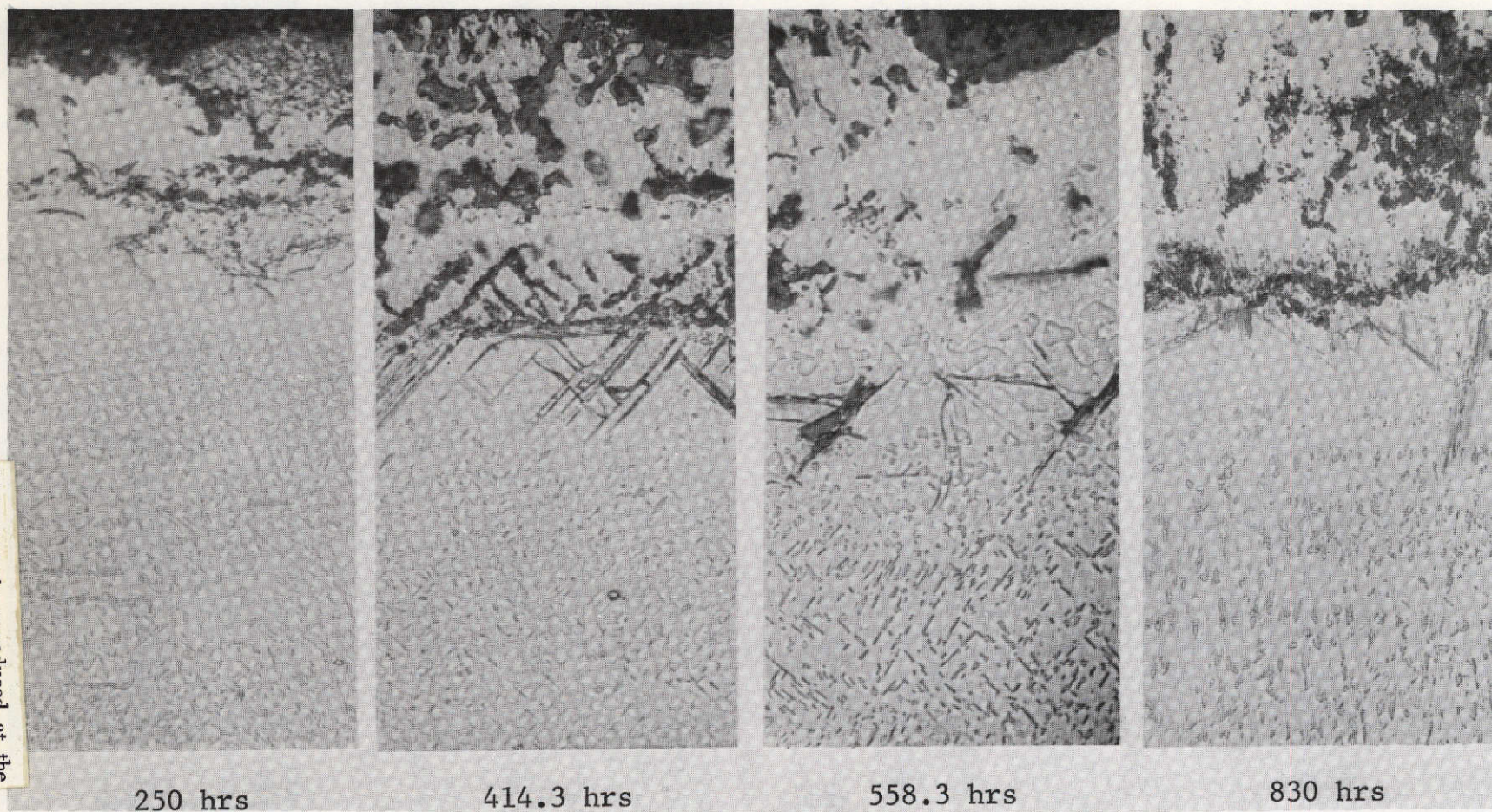


Figure 21 Micrographs of longitudinal sections from NiCrAlY coated NiTaC-13 burner rig oxidation pins after cycling 93° to 1093°C for the specified times. Substrate is at bottom. 500X

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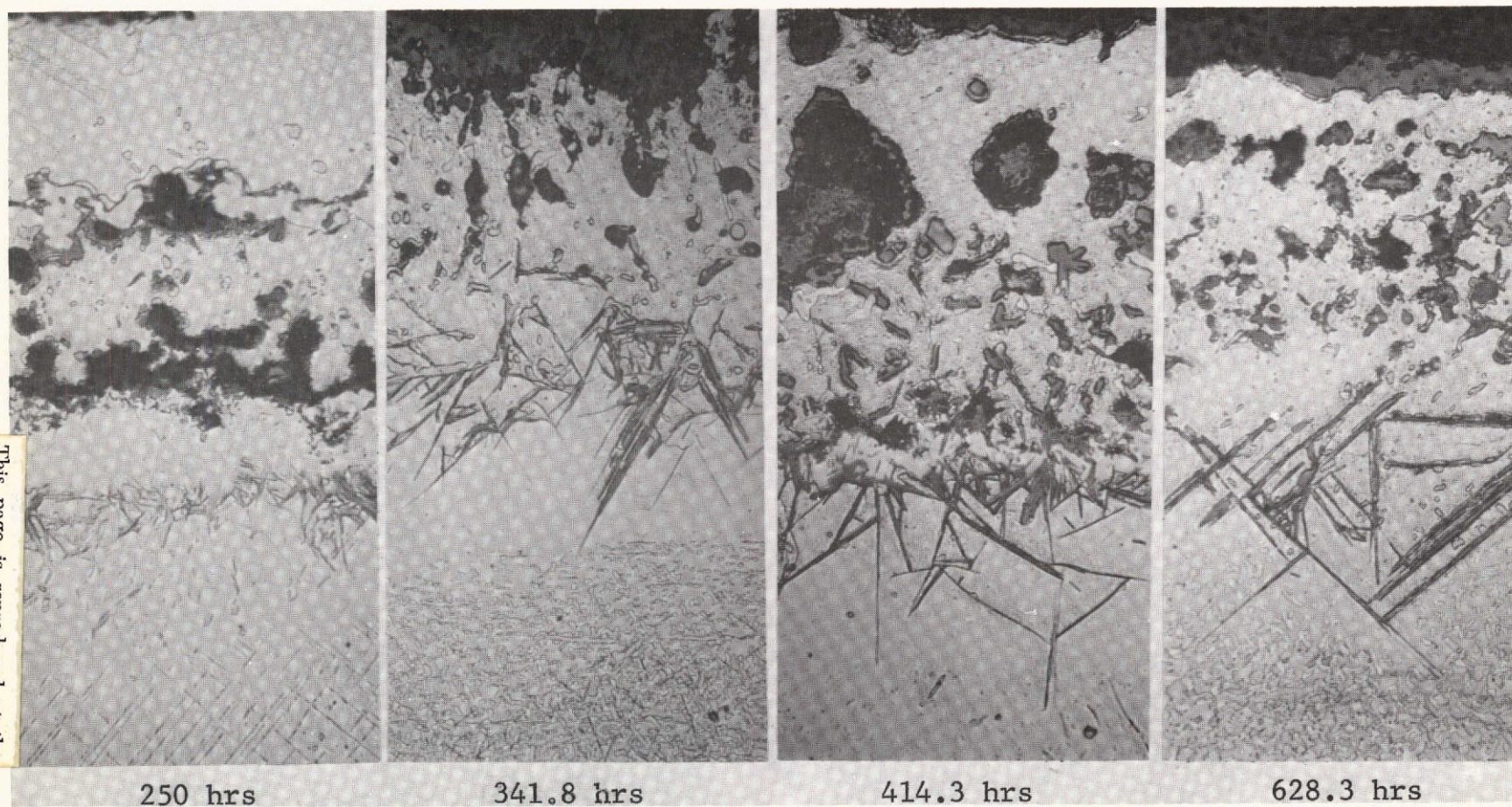


Figure 22 Micrographs of longitudinal sections from duplex coated NiTaC-13 burner rig oxidation pins after cycling 93° to 1093°C for the specified times. Substrate is at bottom. 500X

3. Burner Rig Exposure of Test Bars

Observations made on the cyclic burner rig pins were used to decide on cyclic burner rig exposure times for mechanical test bars. Ten bars were prepared for each of the following conditions:

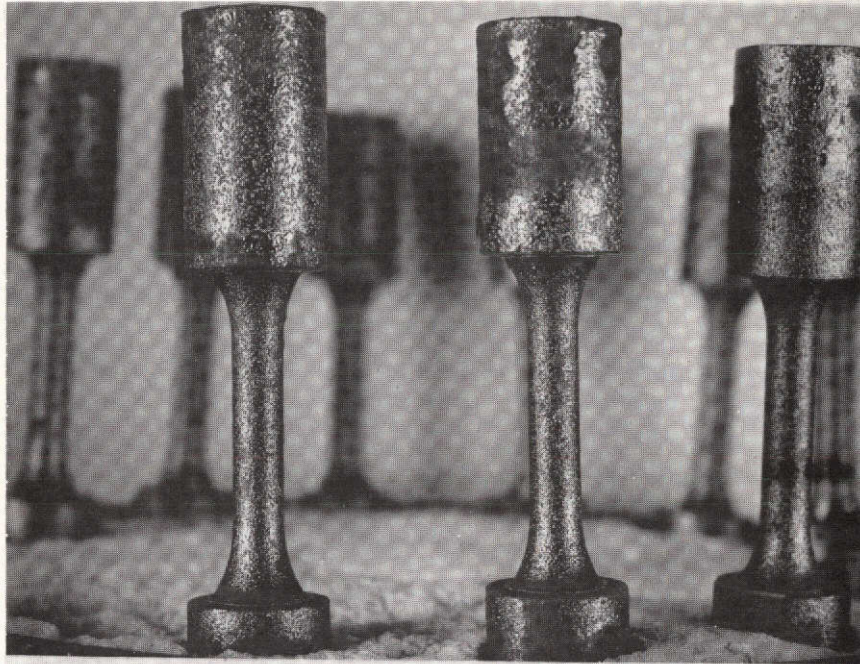
- (a) uncoated NiTaC-13, 48 hours of cycling;
- (b) NiCrAlY coated NiTaC-13, 150 hours of cycling;
- (c) NiCrAlY coated NiTaC-13, 500 hours of cycling;
- (d) duplex coated NiTaC-13, 150 hours of cycling;
- (e) duplex coated NiTaC-13, 250 hours of cycling.

So that mechanical properties could be compared after burner rig cycling for the same time for uncoated and coated bars, several additional uncoated bars were cycled for 100 and 150 hours.

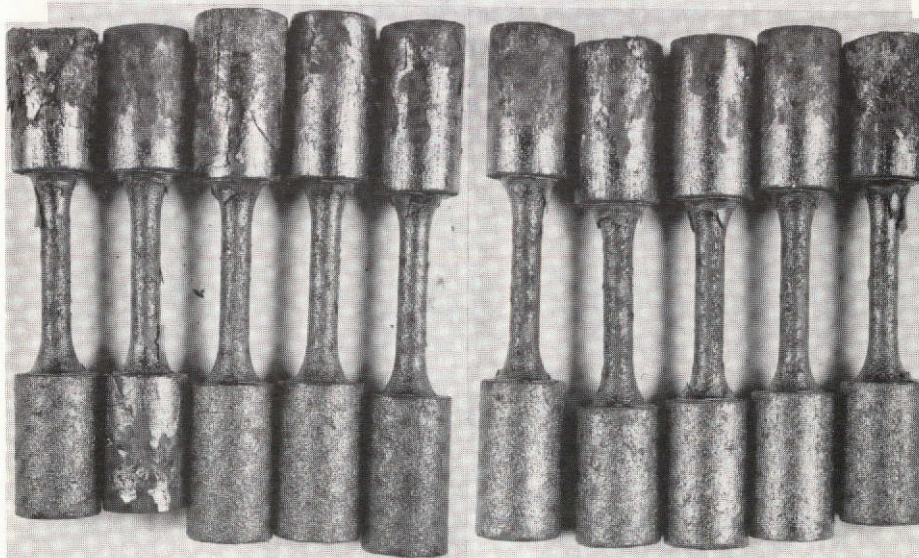
Macrographs of the 48-hour uncoated test bars are shown in Fig. 23. Machined bars had 0.699 cm diameter shoulders and a 0.254 cm diameter gauge, and the gauge is constant in cross-section for the center 0.953 cm with a 0.635 cm radius to the shoulder. The shoulder-to-shoulder distance that results is 1.60 cm. Bars are shown mounted in the burner rig fixture after 24 hours and unmounted after 48 hours. Heavy spalling of the oxide is evident.

Because of the heavy spalling noted on test bars and pins of bare NiTaC-13, it was realized that the support roots and shoulders of mechanical test bars would be severely degraded in longer exposure cycling. For this reason, a commercially available oxidation resistant tape was used to protect root and shoulders of the bars. This required a dry hydrogen heat treatment at 1121°C for 10 minutes to obtain coating bond. Tape coated-shoulder bars are shown in Fig. 24 after 100 and 150 hour burner rig exposures. Gauge diameters were reduced from an initial 0.254 cm to <0.2 cm after 100 hours and <0.18 cm after 150 hours. Spalling occurred in gauge centers, but the tape coating seemed to prevent complete spalling, but not oxidation, of the remainder of the gauge. The tape coating itself was oxidized, but not so severely as to prevent support of the sample in mechanical testing. Before testing, the support roots were machined to insure good seating in test grips.

NiCrAlY coated NiTaC-13 bars are shown in Fig. 25 after 150 and 500 hour cyclic burner rig exposures. Almost no root attack was seen in the 150 hour samples. This is significant because the line-of-sight nature of the vapor deposition process resulted in a 25 μ m coating on roots, compared to a 75 μ m coating on shoulders and gauges. Note the reduction of cross-section for the uncoated shoulder section that was in the sample holder during coating. Because of this attack, it was decided to tape coat these regions for 500 hour



(a)



(b)

Figure 23 Uncoated test bars after burner rig exposure, 93° to 1093°C.

(a) Mounted in burner rig fixture; after 24 hr (7 cycles) exposure. 2.5X

(b) After 48 hr (15 cycles) exposure. 1.5X

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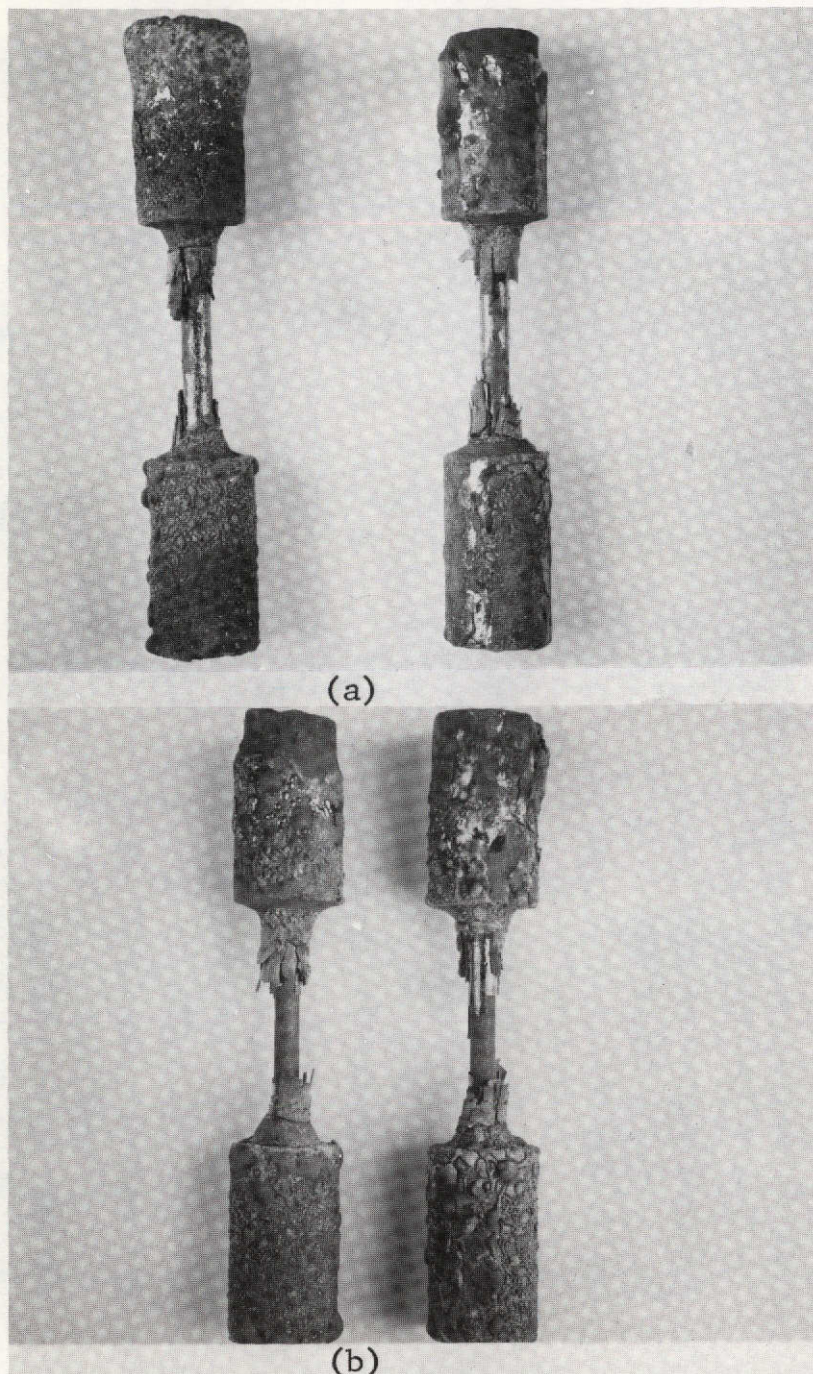


Figure 24 Test bars with gauge uncoated; heads and roots coated with oxidation resistant tape, 93° to 1093°C.
 (a) 100 hr (31 cycles); (b) 150 hr (47 cycles).

2X

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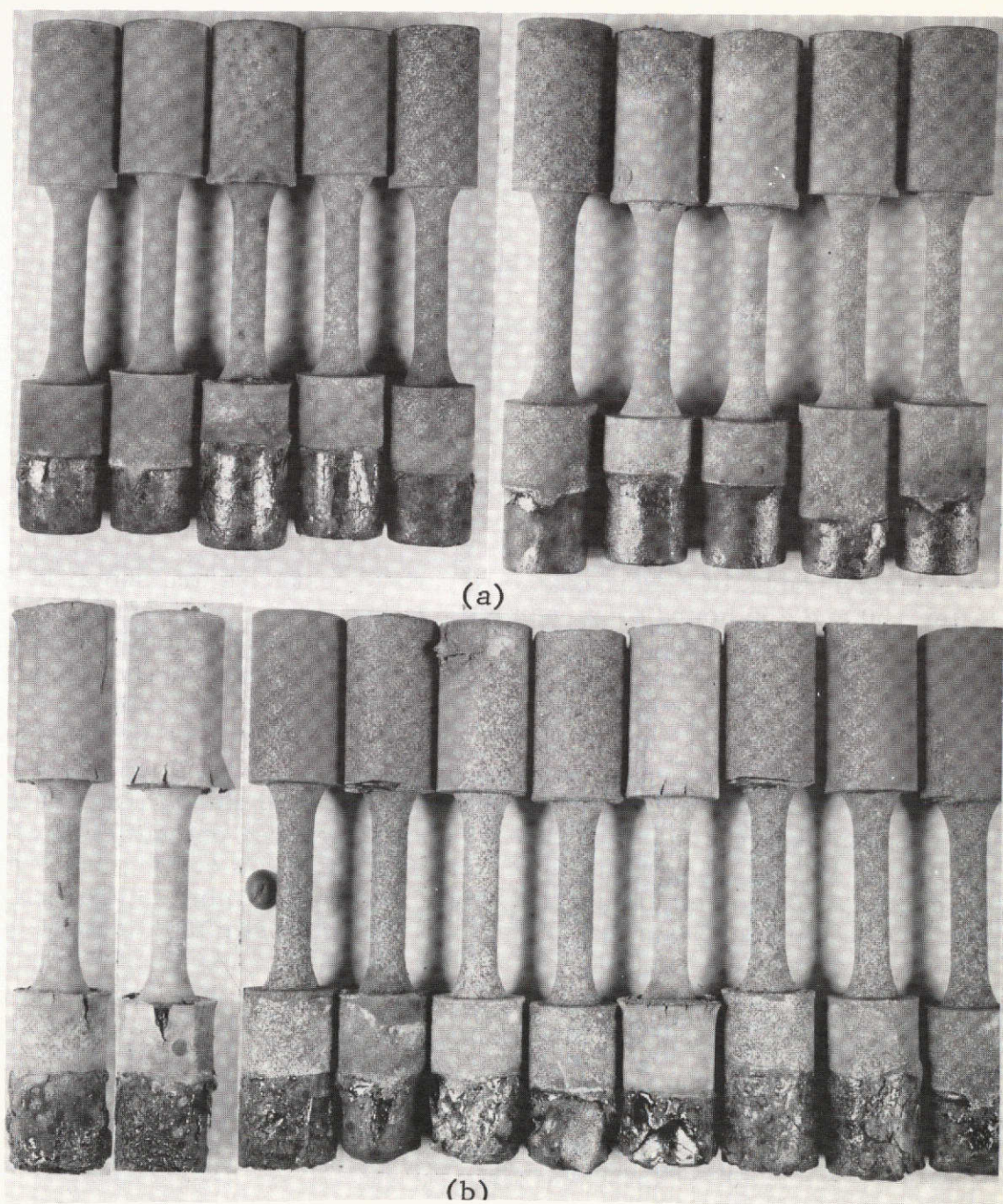


Figure 25 Exposed (93° to 1093°C) NiCrAlY coated test bars.

2X

(a) Exposed 150 hr (44 cycles for the 5 bars at the left, 47 cycles for the remainder); (b) The two bars at the left were removed after 190 hr (55 cycles), the fourth bar from the right was removed after 352 hr, and the rest were cycled for 500 hr (143 cycles).

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cycling to prevent oxidation down the shoulder-coating interface that might degrade the test bar. This was the same tape used on bare pins in Fig. 24. For the 500 hour burner rig samples shown in Fig. 25b, the tape coat has prevented NiCrAlY coating peeling due to interfacial attack, although the tape coat has been oxidized extensively. Some root attack is noted on a number of 500 hour cycled bars, but the coating in gauge regions is in excellent condition. Two bars were removed at 190 hours because of severe attack in the gauge. These samples had been coated simultaneously, and there had been an abnormality during that particular coating run. Because of arcing of the electron gun during deposition, the samples had to be cooled to room temperature, the chamber opened to atmosphere and gun problems corrected, the chamber re-evacuated, and the samples reheated before coating could be completed. This interruption may be responsible for the poor performance of these two test bars. One bar was removed after 352 hours of exposure. The reason for removal was substantial root attack, although the gauge coating showed no deterioration.

Macrographs of duplex coated NiTaC-13 test bars are shown in Fig. 26 after 150 and 250 hours of burner rig cycling. After 150 hours, root attack was evident in nine of ten bars, and was severe in four bars so that peeling of the coating occurred along the shoulder-coating interface. Gauge coatings were in excellent condition, comparable to the NiCrAlY coatings. For this reason, the tape coat mentioned previously was used to give added protection to test bar roots for longer exposure cycling. Again, the tape coat prevented severe interfacial attack in the shoulder regions, thus avoiding coating peeling. Of the samples scheduled for the 250 hour exposure, one suffered coating failure at 137 hours. One of the remainder showed a coating crack at the end of cycling. The other eight bars showed the typical mottled, roughened surface in the gauge similar to that observed on test pins at about 200-250 hours.

C. Stress-Rupture Effects of Cyclic Oxidation

1. Stress-Rupture Behavior of As-Solidified NiTaC-13

a. Parametric Relations

A total of 17 stress-rupture tests have been performed to characterize bare NiTaC-13. Four tests were performed in argon between 1024° and 1093°C on as-directionally solidified (as D.S.) NiTaC-13, and eleven tests were performed in air between 871 and 1093°C. Since it was felt that environmental effects on stress-rupture behavior would be negligible at temperatures where oxidation was slow, there are no argon tests in the regime of 871°C. Also, two tests were performed on bars heat treated three hours at 1160°C to determine the effect of heat treatment on properties. All coated test bars were given this treatment to insure coating-substrate bonding.

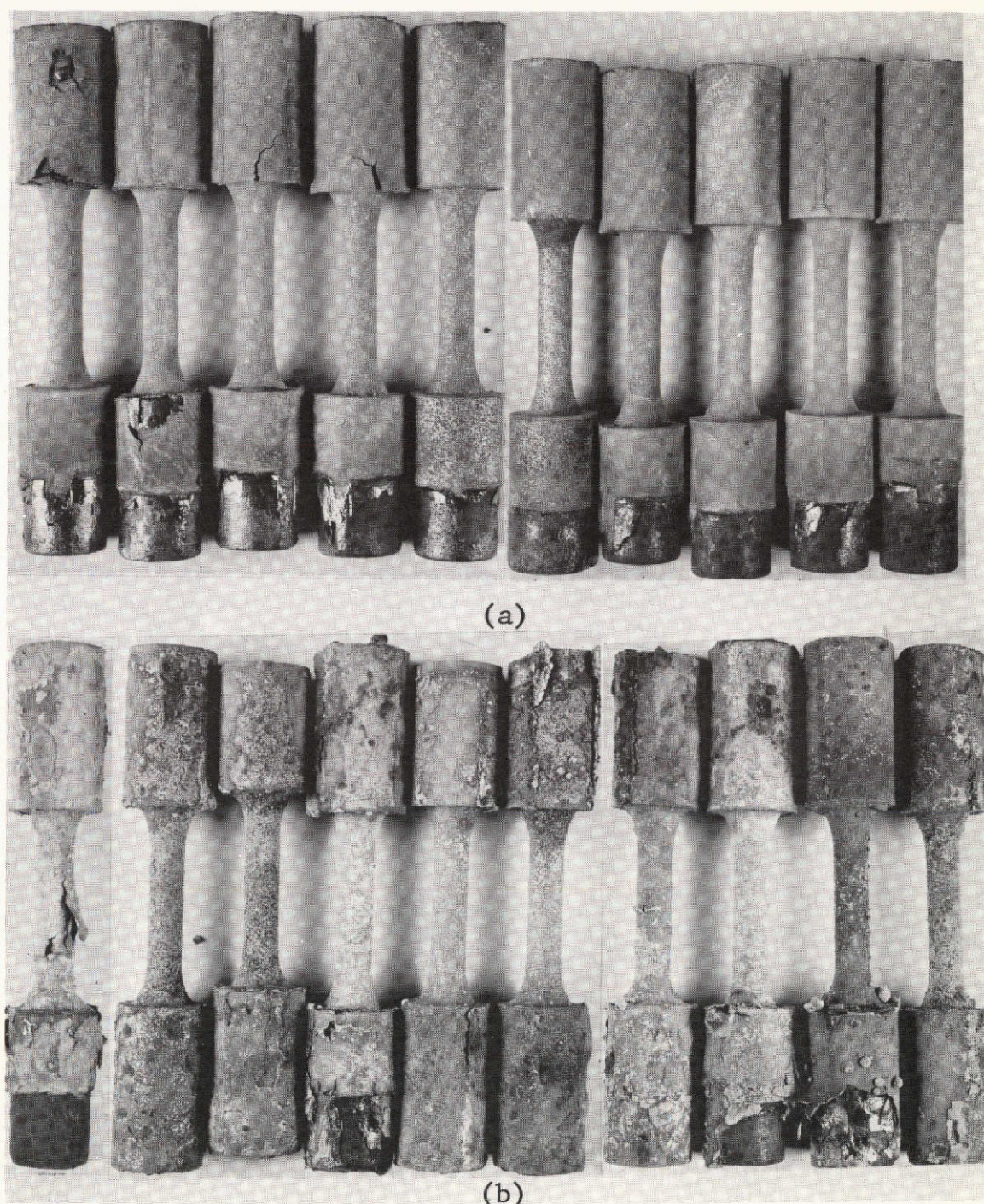


Figure 26 Exposed (93° to 1093°C) duplex coated test bars. 2X
 (a) All bars were cycled 150 hr (44 cycles for the 5 bars at left, 47 cycles for the others); (b) The bar at left was removed after 137 hr; the others after 249.5 hr (73 cycles).

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TABLE III

Stress-Rupture Behavior of as Directionally Solidified NiTaC-13

<u>Stress MN/m²</u>	<u>Temp. (°C)</u>	<u>Life (hrs)</u>	<u>Larson-Miller Parameter (C=20)</u>	<u>Condition</u>
220.5	1024	203.74	52.09	as-solidified, argon-tested
158.5	1066	186.58	53.67	" "
137.8	1093	171.25	54.69	" "
120.6	1093	197.77	54.85	" "
413.4	913	123.64	47.17	" air-tested
379.0	927	129.27	47.76	" "
220.5	996	145.44	50.64	" "
220.5	1024	85.25	51.21	" "
158.5	1038	133.03	52.21	" "
158.5	1052	93.66	52.40	" "
158.5	1066	67.25	52.60	" "
137.8	1093	44.55	53.26	" "
110.2	1066	225.11	53.87	" "
110.2	1079	127.40	53.83	" "
110.2	1093	85.53	53.95	" "
482.3	871	288.05	46.27	heat treated, 3 hrs, "
134.4	1093	42.37	53.20	1160°C, in argon "

In Table III, baseline rupture properties are given for the tests listed above. The parameter is the Larson-Miller parameter, $P = T [1.8 \times (°C + 273)] \times [20 + \log_{10} t(\text{hrs})]$.

These data are plotted in Fig. 27. As the figure shows, the three-hour argon heat treatment has no noticeable effect on stress-rupture behavior in air. Using the 13 data points for tests in air, the line for a simple polynomial equation has been drawn in the figure. The equation of the line is:

$$P = 57,460 - 243 \cdot S + 1.2 S^2,$$

where S is stress in units of $\text{MN/m}^2/6.89$ (1 ksi). The 3σ limit assuming a Gaussian distribution is ± 0.500 and is shown as the shaded region in the

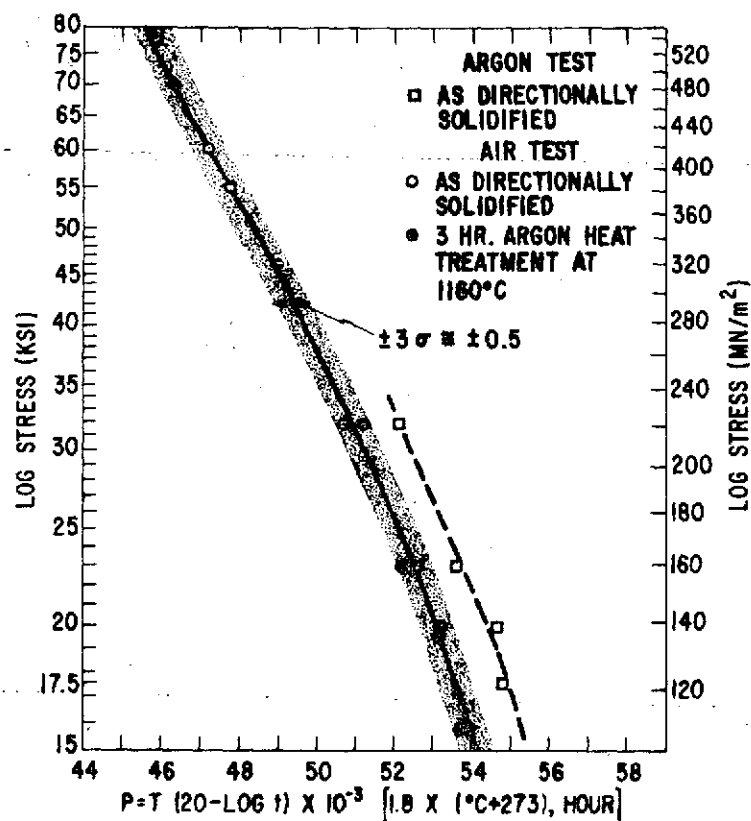


Figure 27 As-directionally solidified base line stress rupture data for NiTaC-13; stress versus Larson-Miller parameter.

figure. A similar line has been drawn for the argon data with the equation:

$$P = 58,965 - 245 S + 0.9 S^2.$$

For low stresses and high temperatures, the air and argon lines are close to parallel and separated by 1.5 parameters.

b. Metallographic Examination

Representative scanning electron micrographs of rupture bars of as-solidified NiTaC-13 are shown in Fig. 28 (air test, 913°C) and Fig. 29 (argon test, 1093°C). For the 913°C stress-rupture air test (Fig. 28), the fracture surface is irregular microscopically and flat macroscopically. Carbide fiber fractures occur in the gauge well away from the fracture surface and some fiber fractures are associated with intersections of fibers with platelets. Platelets were discussed in detail in Section B-2. Platelets present are small in diameter, probably less than 5 μm . In the head of this test bar, almost no platelets are observed. Stress apparently accelerates platelet precipitation.

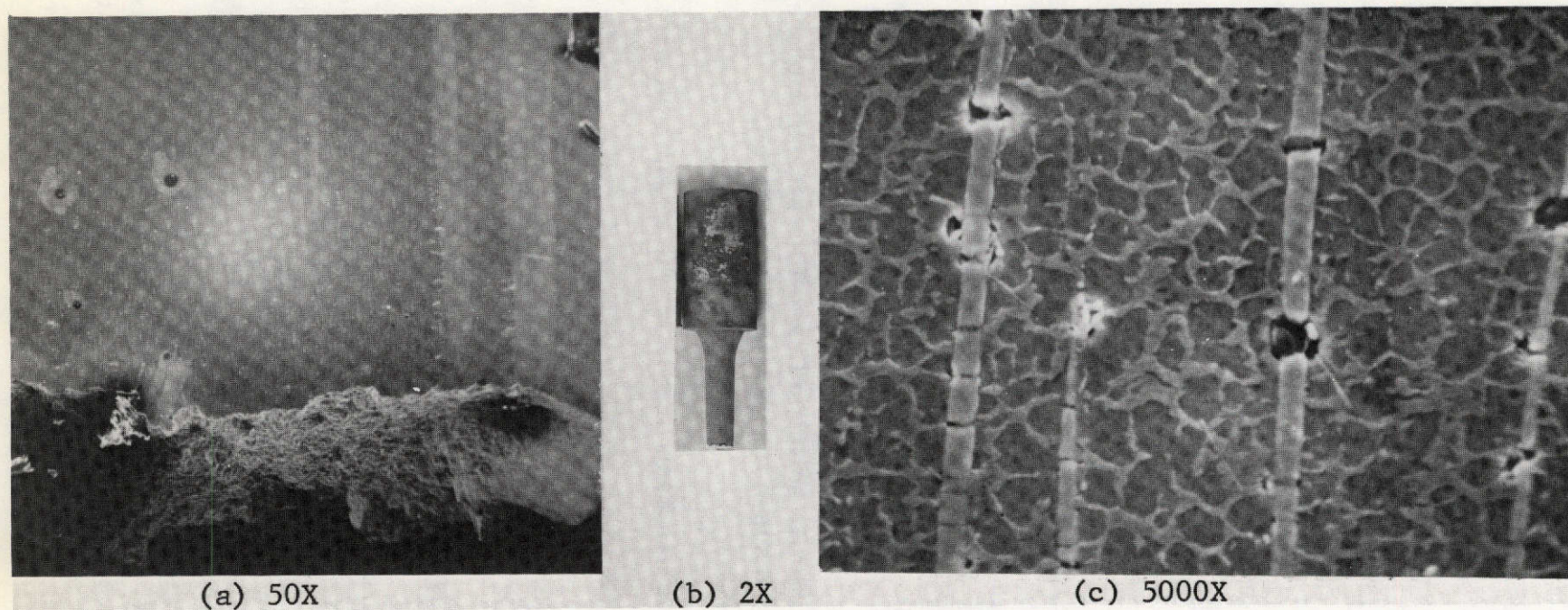


Figure 28 Macro and micrographs of as-directionally solidified NiTaC-13 stress rupture bar: 913°C/413.4 MN/m²/123.64 hrs life. Longitudinal section through rupture surface is shown in (a), (b) shows fracture orientation, and (c) shows microstructure near fracture surface.

The structure resulting after 1093°C stress rupture in argon is shown in Fig. 29. Substantial reduction in area occurs before fracture, and the structure near the fracture surface (Fig. 29c) bears little resemblance to the as-solidified structure. Figure 29(d-i) shows structure in the essentially unstressed head, in the gauge, and near the fracture surface. Short platelets are seen in the shoulder, but the γ' morphology is essentially the same as before test. Platelets in the gauge away from the fracture surface are considerably larger. Also, the γ' phase has coarsened and agglomerated in the direction perpendicular to the applied tensile stress. This is probably the same effect noted for conventional superalloys.⁽⁶⁾ The uniaxial strain causes loss of coherency of $\gamma - \gamma'$ interfaces parallel to the stress axis, and agglomeration results in increases in the length of coherent interface (perpendicular to the stress axis) at the expense of strained interfaces. Near the fracture surface, carbide fibers have been broken and rotated by matrix flow. The platelet phase also has been broken, and considerable agglomeration of γ' has occurred.

2. Stress-Rupture Behavior of Cyclically Burner Rig Exposed Bare NiTaC-13

a. Parametric Relations

Uncoated NiTaC-13 cycled for 48, 100, and 150 hours to 1093°C in the Lynn burner rig was rupture tested at 871°C and 1093°C. Also, several bars were vacuum encapsulated at 10^{-7} torr in quartz and cycled in the cyclic furnace oxidation test. Data for these tests are given in Table IV and are plotted in Fig. 30.

The stresses given in the table are calculated from the actual diameter after cycling. Figure 30 shows about a 0.5 parameter loss from baseline data after 48 hours of burner rig cycling. Samples cycled for 100 and 150 hours in the burner rig show substantially greater losses, 1.5-2 parameters. However, much of this loss may be due to surface cracks and other irregularities resulting from oxidation and spalling during burner rig cycling. Data for bars furnace cycled in vacuum for 150 hours and tested in air show about a parameter loss from the air as D.S. baseline, nearly a parameter better than samples burner rig cycled 150 hours.

The sample vacuum cycled 150 hours and argon tested shows about a one parameter loss from the argon as D.S. baseline. This, plus the vacuum cycled air tested data, indicate that the alterations caused in NiTaC-13 by a simulated jet engine cycle repeated 150 times results in about a parameter loss in properties.

As was noted in Section B-3, the bars cycled in air had substantial reduction in cross-section due to oxidation and spalling: 0.25 cm to >0.23 cm after 48 hours, to <0.20 cm after 100 hours, to <0.18 cm after 150 hours.

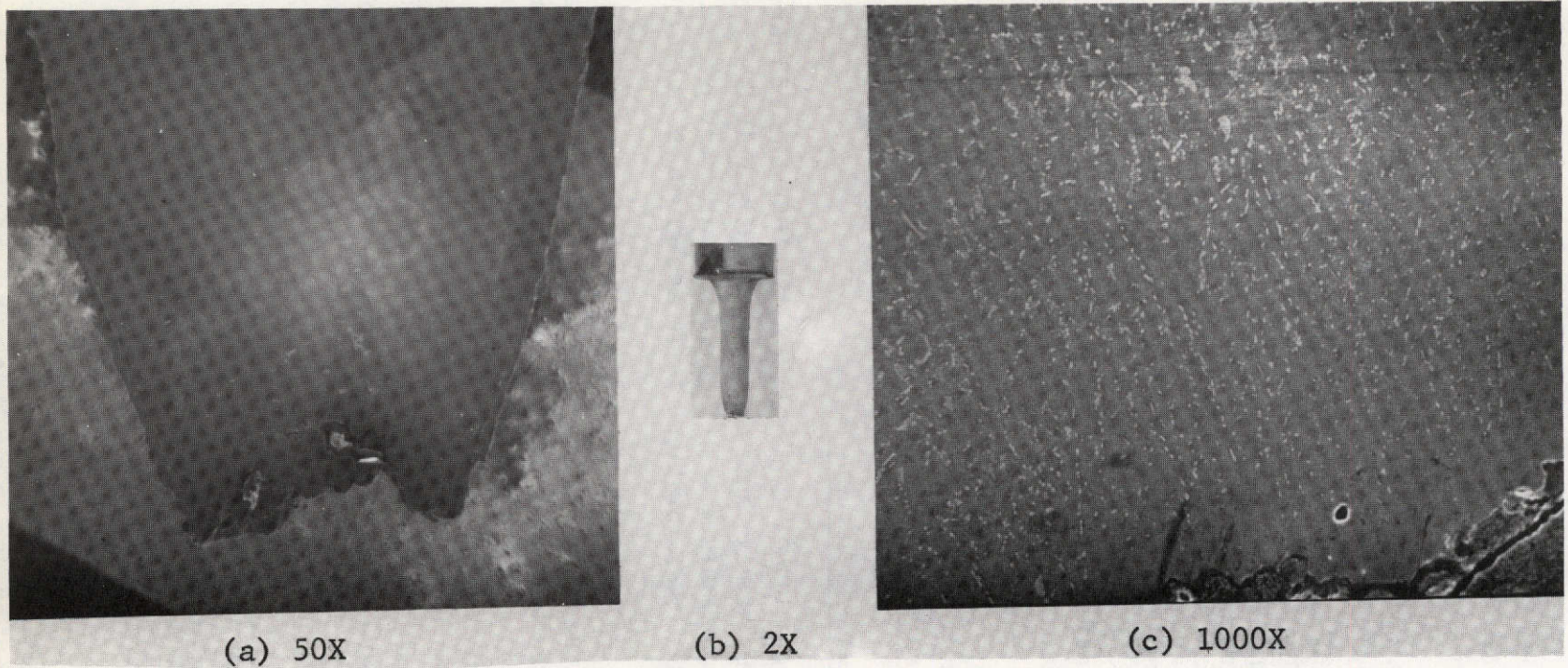


Figure 29 Macro and micrographs of as-directionally solidified NiTaC-13 stress rupture bar: 1093°C/137.8 MN/m²/171 hrs life. Magnifications as shown. Longitudinal section through rupture surface is shown in (a), (b) is for orientation of the other photographs, and (c) shows the microstructure near the fracture surface.

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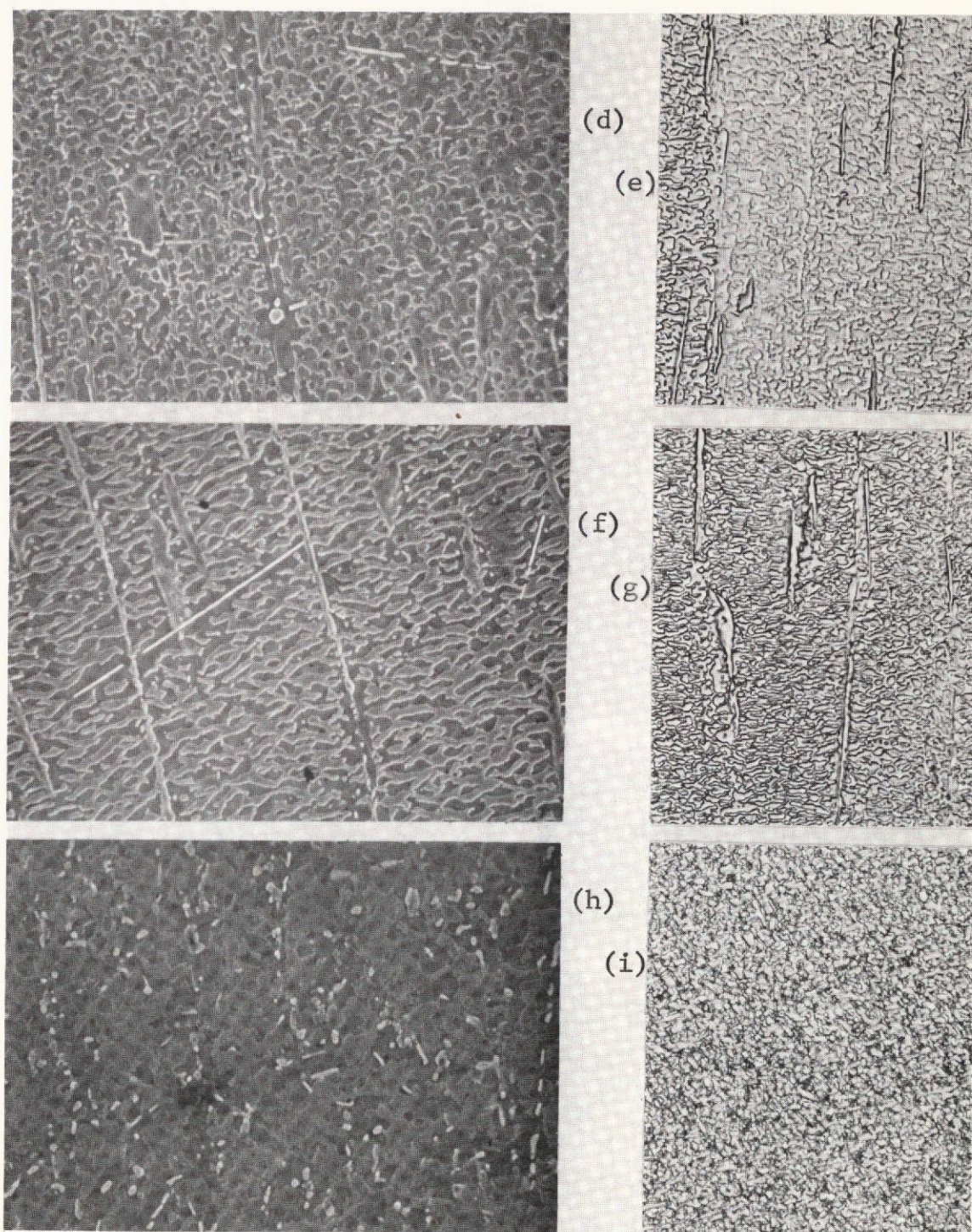


Figure 29 (continued): Micrographs from longitudinal section in head (d, e), gauge (f, g), and gauge near fracture surface (h, i), of NiTaC-13 stress rupture bar: 1093°C/137.8 MN/m²/171 hrs life. Magnification of SEM photographs is 2000X (d, f, h), and of light micrographs is 750X (e, g, i).

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TABLE IV

Stress-Rupture Behavior of Cyclically Exposed
(93° to 1093°C - Burner Rig or Vacuum) Bare NiTaC-13

<u>Stress</u> <u>MN/m²</u>	<u>Temp.</u> <u>(°C)</u>	<u>Life</u> <u>(hrs)</u>	<u>Larson Miller</u> <u>Parameter (C=20)</u>	<u>Condition</u>
482.3	871	133.73	45.58	48 hr cycle: 1093°C, air-tested
465.1	871	178.91	45.84	48 hr cycle: 1093°C, air-tested
120.6	1093	43.13	53.22	48 hr cycle: 1093°C, air-tested
110.2	1093	61.11	53.59	48 hr cycle: 1093°C, air-tested
465.1	871	80.41	45.12	100 hr cycle: 1093°C, air-tested
110.2	1093	33.41	52.95	100 hr cycle: 1093°C, air-tested
465.1	871	27.62	44.17	150 hr cycle: 1093°C, air-tested
110.2	1093	22.61	52.53	150 hr cycle: 1093°C, air-tested
465.1	871	104.83	45.36	{ 150 hr cycle: 1093°C, air-tested vacuum encapsulated, air-tested }
110.2	1093	43.87	53.24	
110.2	1093	45.51	53.28	as above, but 500 hr cycle, air-tested
110.2	1093	116.48	54.28	as above, but 150 hr cycle, argon-tested
110.2	1093	63.57	53.64	as above, but 500 hr cycle, argon-tested

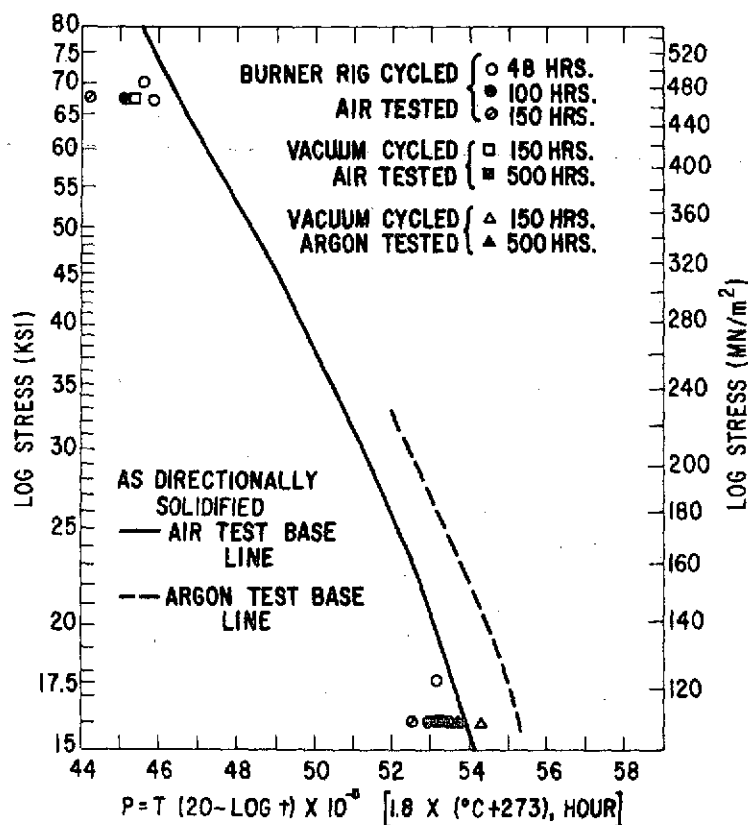
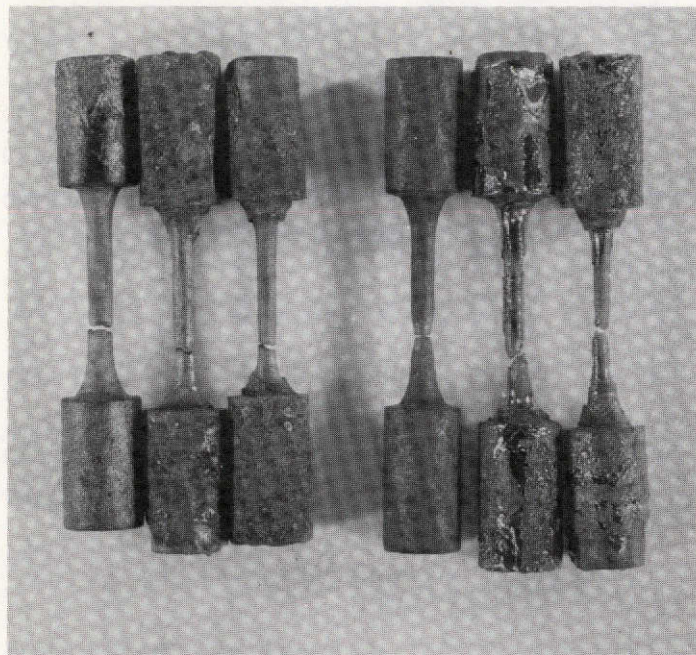


Figure 30 Effects of cyclic burner rig or vacuum exposure (93° to 1093°C) on NiTaC-13 stress rupture; stress versus Larson-Miller parameter.

Thus, bars cycled 150 hours have approximately one-half their original areas. The need for oxidation protection is obvious if stress is considered in terms of original rather than final diameter.

b. Structure

Macrographs are shown for the uncoated bars after failure in Fig. 31. This can be compared to Figs. 23 and 24 after cycling. Micrographs of the structures present in a 871°C stress-rupture test bar previously cycled for 150 hours to 1093°C are shown in Fig. 32. The fracture surface is quite angular, unlike that shown in Fig. 28. At higher magnifications, it can be seen that the angularity of the fracture surface closely parallels the intersection of platelets with the polished surface. Platelets were discussed in detail in Section B2. Figure 32c shows a region where fibers have broken. Some fractures appear to be associated with platelet intersections. In several areas in that micrograph, some cracks are seen forming at γ' -platelet interfaces in the absence of a fiber break in the plane of polish. Figure 32 suggests the following sequence as a possible (speculative) description of crack growth within individual eutectic grains: fibers break where stress concentrations



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Figure 31 2X macrographs of uncoated NiTaC-13 failed stress rupture bars. From the left, burner rig cycled 93° to 1093°C: 48 hrs cycling, 871°C test; 100 hrs cycling, 871°C test; 150 hrs cycling, 871°C test; 48 hrs cycling, 1093°C test; 100 hrs cycling, 1093°C test; and 150 hrs cycling, 1093°C test.

occur, often at an intersection with a platelet. Cracks then grow by extending from the fiber-platelet intersection along the γ' -platelet interface. Cracks grow and intersect until catastrophic failure occurs.

Microstructures after stress rupture at 1093°C of uncoated NiTaC-13 cycled in the burner rig are similar to those of uncycled NiTaC-13 (as in Fig. 29). More platelets are present and the γ' morphology is essentially the same as that shown in Fig. 32, but matrix flow and necking are similar to that of uncycled material.

c. Thermal Cycling

Before considering coated bar stress rupture behavior, it is important to put the results for uncoated NiTaC-13 in some perspective. Figure 30 implies a full parameter loss occurs along the entire parameter curve. However, it must be remembered that cycled samples tested at 871°C have been altered by cyclic oxidation at 1093°C. In actual jet engine use, the blade regions designed for 871°C use would never see 50 minutes exposure to 1093°C per hour, the time the test bars were exposed in a single cycle. A stress-parameter curve for cyclically oxidized material is expected to follow the baseline curve more closely if the maximum cycle temperature is the same as the stress-rupture test temperature.

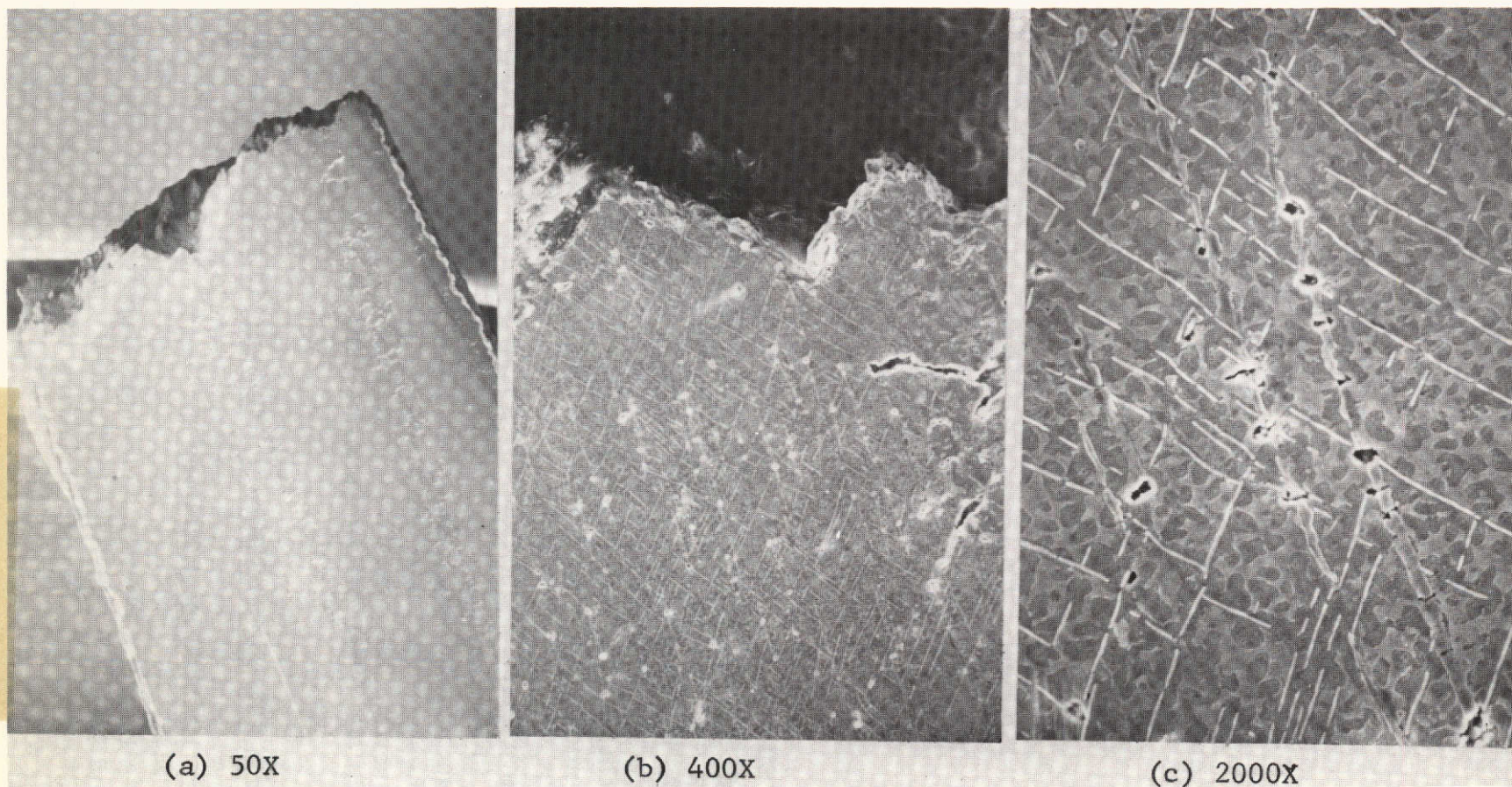


Figure 32 Micrographs from longitudinal section through rupture surface of uncoated NiTaC-13 bar. Bar was previously cyclically oxidized (93° to 1093°C in a burner rig) 150 hrs and then was tested at 871°C/ 465.1 MN/m²/27.62 hrs life.

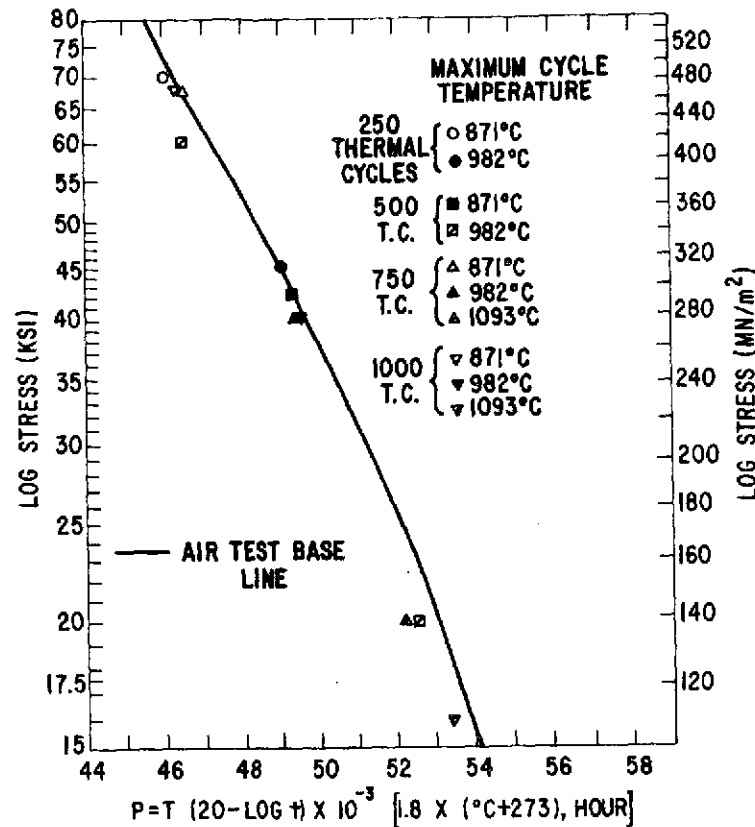


Figure 33 Effects of thermal cycling on NiTaC-13 stress rupture; stress - versus Larson-Miller parameter. All tests were performed at the maximum cycle temperature, except for one (\square at 413.4 MN/m²) which was cycled to 1093°C and tested at 871°C.

Such behavior was seen for NiTaC-13 previously.⁽⁸⁾ In that study, ingots were subjected to a 20-minute cycle -- 10 minutes heating to temperature (either 1093°, 982°, or 871°C) and 10 minutes cooling to below 93°C. After cycling, test bars were machined from the ingot material. Ten data points in Fig. 33 and in Table V are for bars tested at the same temperature to which the ingot had been cycled. Material cycled to and tested at either 871° or 982°C have lifetimes equivalent to the baseline values. Samples cycled to and tested at 1093°C show approximately 0.5 parameter loss. The sample cycled to 1093°C and tested at 871°C fell off the baseline, unlike material cycled and tested at 871°C.

3. Stress Rupture of Burner Rig Cycled Coated NiTaC-13

a. Parametric Relations

Data for NiCrAlY and duplex coated NiTaC-13 are listed in Table VI and shown in Fig. 34. It should be noted that some of these data are for material containing banded structure in the gauge length. Metallographic screening before making specimens failed to identify the band in this ingot.

TABLE V

Stress-Rupture Behavior for NiTaC-13 After Thermal Cycling
(20 minute cycle) 93° to 1093°C

Stress MN/m ²	Temp. (°C)	Life (hrs)	Larson Miller Parameter (C=20)	Condition
482.3	871	219.92	46.03	250 cycles to 871°C
465.1	871	382.79	46.52	748 cycles to 871°C
465.1	871	333.55	46.40	1000 cycles to 871°C
310.1	982	49.06	49.02	252 cycles to 982°C
292.8	982	57.68	49.18	500 cycles to 982°C
275.6	982	71.65	49.39	750 cycles to 982°C
275.6	982	77.51	49.47	1000 cycles to 982°C
137.8	1093	25.16	52.65	500 cycles to 1093°C
137.8	1093	18.84	52.34	750 cycles to 1093°C
110.2	1093	55.20	53.49	1000 cycles to 1093°C
413.4	913	59.18	46.48	500 cycles to 1093°C

Bands seemed to have little effect on behavior at 871°C, while properties at 1093°C were degraded slightly.

If coatings are protective against oxidation and do not influence the behavior of the substrate, stress-rupture properties of as-coated NiTaC-13 are expected to equal the as-D.S. air base line at 871°C and the as-D.S. argon base line at 1093°C. (It is assumed that the air and argon stress rupture properties coincide at 871°C.) Test results for both coatings, as coated and heat treated, fall below the air base line at 871°C and the argon base line at 1093°C. Since heat treated NiTaC-13 is part of the air baseline for uncoated material, it is unlikely that the degradation in properties is due to the heat treatment. Surface structure, faults or brittleness of the coating may be the cause, or it may be due to fiber denuding at the coating-substrate interface during heat treatment.

Following burner rig cyclic exposure, 93° to 1093°C, for 150 hours or more, both coatings show degraded stress rupture properties at 871° and 1093°C, relative to the uncycled coated condition, by about 1 parameter. This is just as was the case for air or argon testing of uncoated uncycled and cycled NiTaC-13, and is apparently a result of microstructural changes unrelated to the coatings being present. Neither coating showed further degradation from short to long cyclic exposure.

TABLE VI

Stress-Rupture Behavior of Burner Rig Cycled (93° to 1093°C)
Coated NiTaC-13

Stress MN/m ²	Temp. (°C)	Life (hrs)	Larson Miller Parameter (C=20)	Condition
482.3	871	173.71	45.81	NiCrAlY, no cycling*
137.8	1093	25.93	52.68	NiCrAlY, no cycling
482.3	871	56.01	44.80	NiCrAlY, 150 hrs cycling
465.1	871	52.35	44.74	NiCrAlY, 150 hrs cycling
120.6	1093	65.24	53.66	NiCrAlY, 150 hrs cycling
110.2	1093	122.50	54.34	NiCrAlY, 150 hrs cycling
465.1	871	52.31	44.74	NiCrAlY, 500 hrs cycling
434.1	871	98.68	45.31	NiCrAlY, 500 hrs cycling
103.4	1093	128.44	54.39	NiCrAlY, 500 hrs cycling
110.2	1093	52.95	53.44	NiCrAlY, 500 hrs cycling*
482.3	871	176.79	45.83	Duplex, no cycling
137.8	1093	49.75	53.37	Duplex, no cycling
124.0	1093	64.19	53.65	Duplex, no cycling
482.3	871	59.45	44.85	Duplex, 150 hrs cycling
465.1	871	71.09	45.01	Duplex, 150 hrs cycling*
120.6	1093	24.38	52.61	Duplex, 150 hrs cycling
110.2	1093	49.89	53.38	Duplex, 150 hrs cycling
465.1	871	89.50	45.22	Duplex, 250 hrs cycling
434.1	871	119.58	45.48	Duplex, 250 hrs cycling
110.2	1093	30.84	52.86	Duplex, 250 hrs cycling
103.4	1093	69.80	53.74	Duplex, 250 hrs cycling

*Banded structure in gauge.

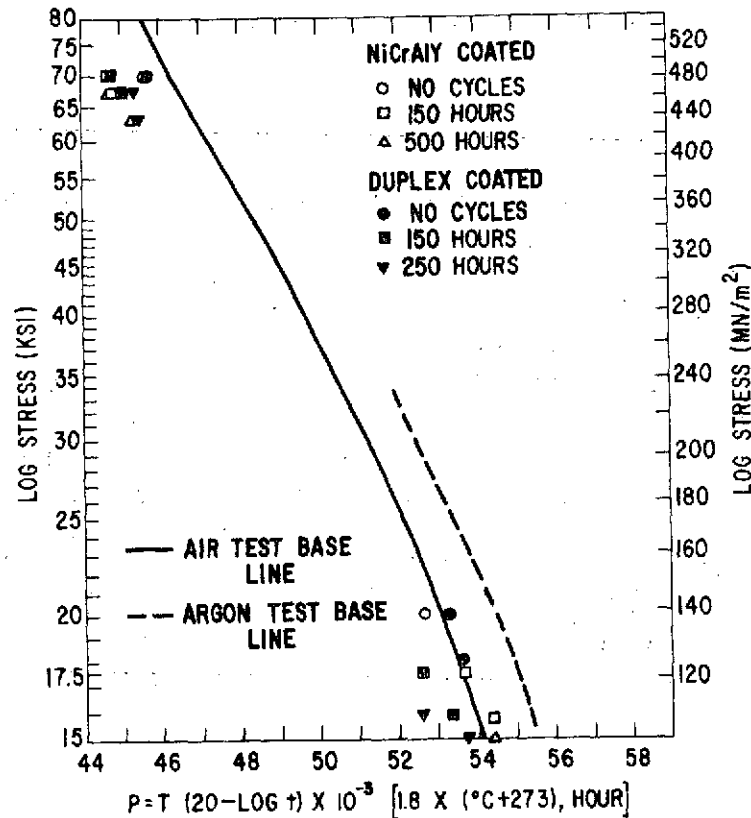


Figure 34 Effects of coatings on stress rupture of cyclically burner rig oxidized (93° to 1093°C) NiTaC-13; stress versus Larson-Miller parameter.

Duplex coated bars were better than NiCrAlY coated bars in stress rupture at 871°C, but the difference is quite small. For a comparison after 150 hours of burner rig cycling, the duplex coated bars lead by 0.16 parameter. No comparison can be made for longer exposure times, since the duplex coated bars had to be removed from the burner rig after 250 hours because of coating degradation.

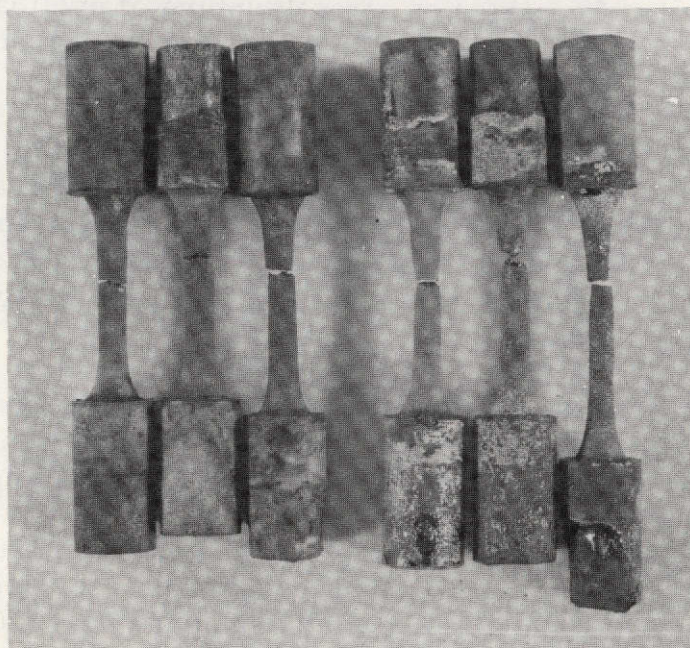
For stress rupture at 1093°C of burner rig cycled coated samples the situation is reversed. Bars coated with NiCrAlY are consistently better than duplex coated bars. After 150 hours of burner rig cycling, NiCrAlY coated bars have rupture lifetimes 2-2.5 times longer (about one parameter greater) than duplex coated bars for the same test conditions. Although the conditions are not completely comparable, duplex coated bars cycled 250 hours were inferior to NiCrAlY coated bars cycled 500 hours by ~0.6 parameters.

In terms of protection against the combined action of stress and environment at 1093°C, NiCrAlY appears to be a superior coating. Duplex coatings offered protection to oxidation during burner rig cycling, but in stress rupture at 1093°C the behavior of cycled duplex coated NiTaC-13 was equivalent to bare NiTaC-13 vacuum furnace cycled and air tested. The cycled NiCrAlY

coated NiTaC-13, on the other hand, had 1093°C stress rupture properties equivalent to bare NiTaC-13 vacuum furnace cycled and argon tested. The NiCrAlY coating was protective during burner rig cycling and stress rupture.

b. Structure

Macrographs of NiCrAlY coated test bars after failure are shown in Fig. 35, and micrographs of a 871°C test in Fig. 36. The coating-substrate bond seems excellent after testing at both 871°C and 1093°C. Figure 36a shows a longitudinal section through the fracture surface with fracture surface at the bottom and the coated edge at the left. Breaks are observed in the coating near the fracture surface, but away from this region the coating appears to be unaffected by stress (Fig. 36b). Figure 36c shows details of the coating, and the absence of the dark, coarse needle-like particles parallel to the platelets noted in oxidation pins (Fig. 21). The coating seems to be more sound than was the case for oxidation pins. Figures 36d and e show details of the substrate after 500 hours of cycling. Phases are coarsening, and γ' may be the matrix phase with γ particles within, as seen in Fig. 36e. The brightest phase is the platelet phase described in Section B2. γ is the second brightest phase, now considerably agglomerated, and the dark matrix is γ' .



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Figure 35 2X macrographs of NiCrAlY coated NiTaC-13 failed stress rupture bars. From the left, 93° to 1093° burner rig cycled: no cycling, 871°C test; 150 hrs cycling, 871°C test; 500 hrs cycling, 871°C test; no cycling, 1093°C test; 150 hrs cycling, 1093°C test; and 500 hrs cycling, 1093°C test.

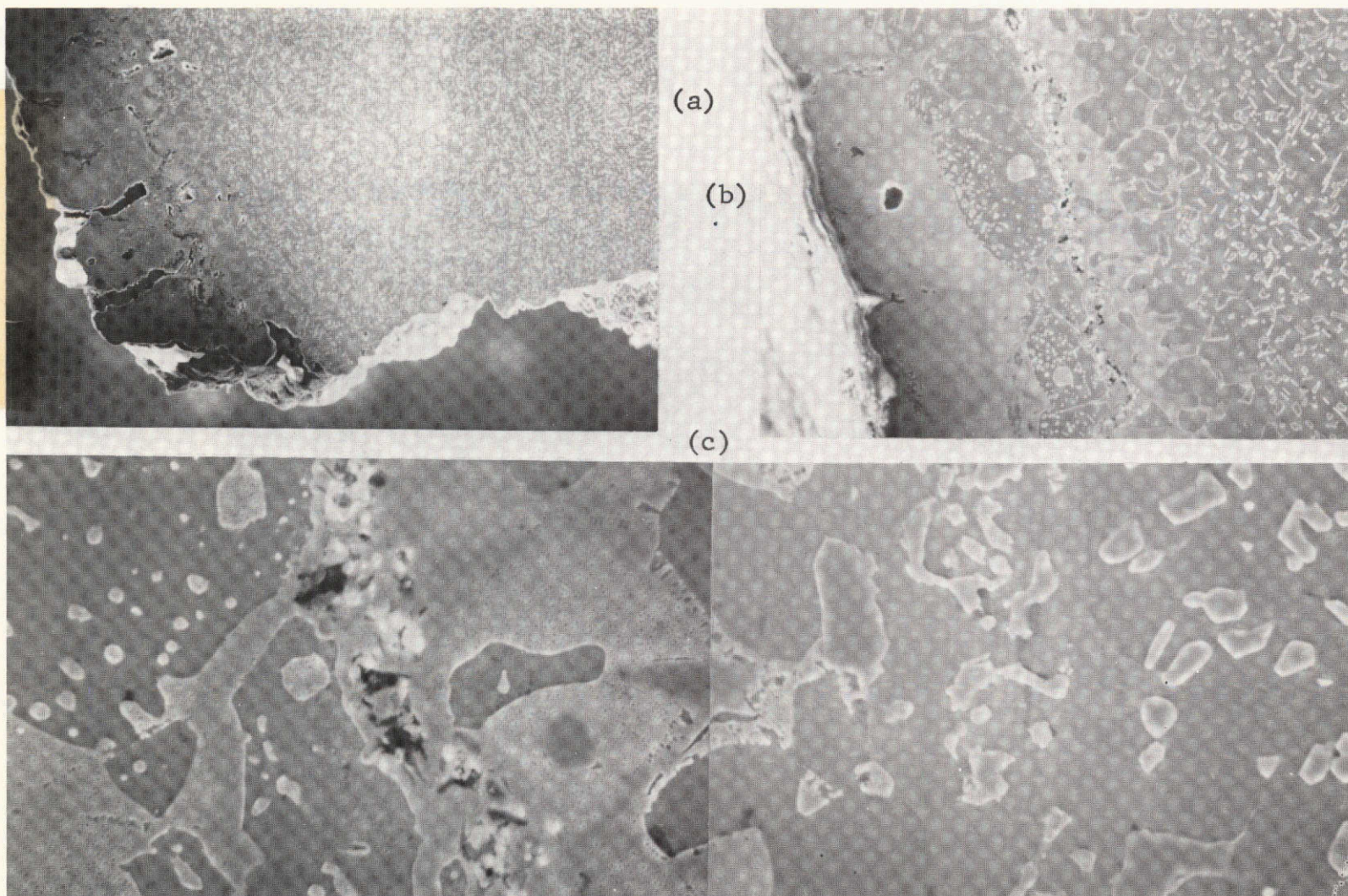
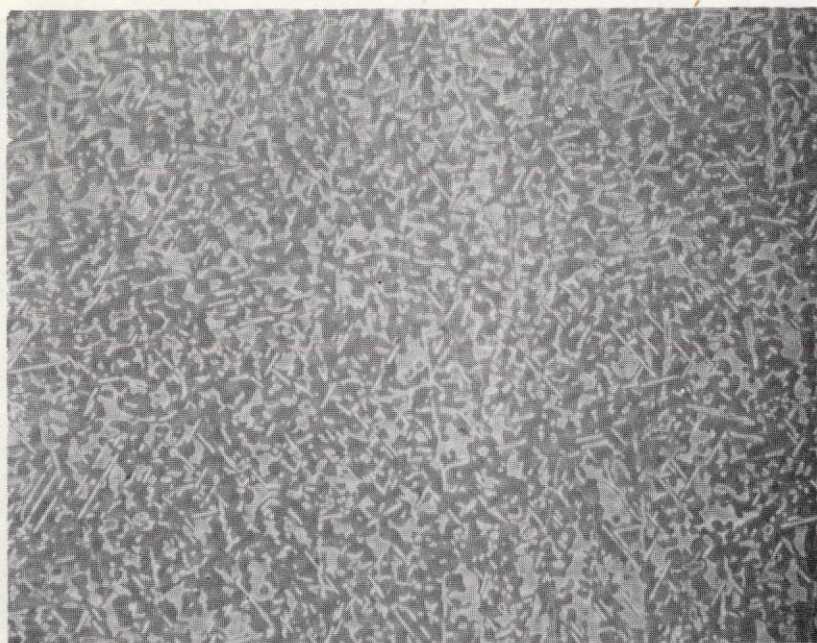
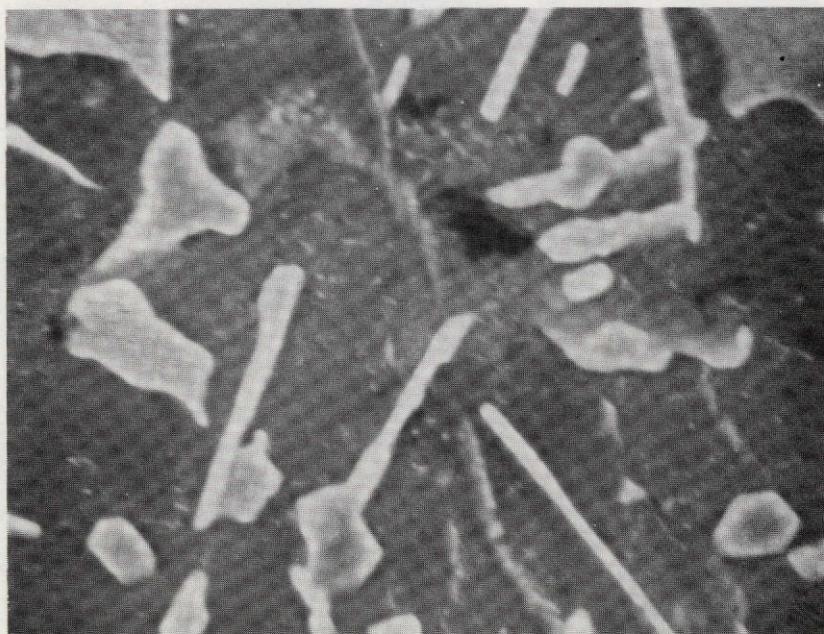


Figure 36 Longitudinal section through a stress rupture bar of NiCrAlY coated NiTaC-13 previously cyclically oxidized 93° to 1093°C in a burner rig for 500 hrs and tested at 871°C/465.1 MN/m²/52.31 hrs life. (a) 400X, (b) 1000X, and (c) 5000X, show features of the coating.



(d)



(e)

Figure 36 (continued): Longitudinal section as before, showing structure in substrate well away from the coating. (d) 1000X, (e) 10,000X.

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Macro and micrographs of duplex coated test bars are shown in Figs. 37 and 38. Separation of coating and substrate has occurred in at least one case at 1093°C after 150 hours of cycling. The micrographs in Fig. 38 are from the second 1093°C stress-rupture test after 150 hours of cycling. No separation of coating and substrate is noted for this sample. Figure 38 b and c show details of the coating. As with NiCrAlY, the needle-like phase is not seen (see Fig. 22).

D. Effects of Cyclic Oxidation on Tensile Behavior

Coated and uncoated test bars were cyclically oxidized in the burner rig at the same time as were identical test bars which were to be tested in stress-rupture. However, whenever samples had to be removed prematurely from cycling because of coating attack, they were used for short-time tensile test rather than for stress-rupture test.

Tests were to be run with a cross-head speed of 0.005 cm/cm/min until fiber failure occurred and then at 0.05 cm/cm/min (effective gauge length is 1.27 cm). However, in none of the tests did a load drop occur, such as might be expected when fibers fail. In practice, the cross-head speed was increased at 2% to 3% elongation. At room temperature, there was only a slight increase in stress when the strain rate was increased. At 871°C and

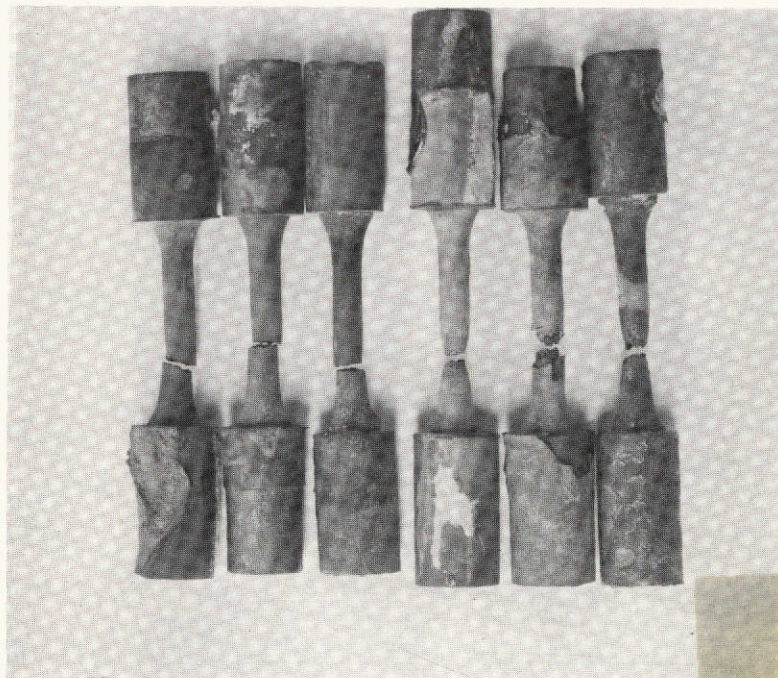
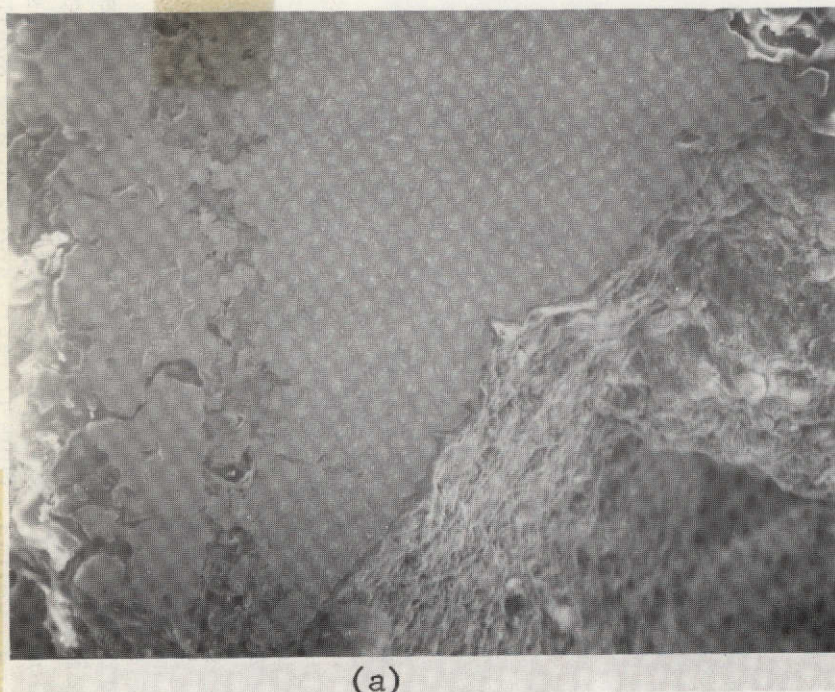
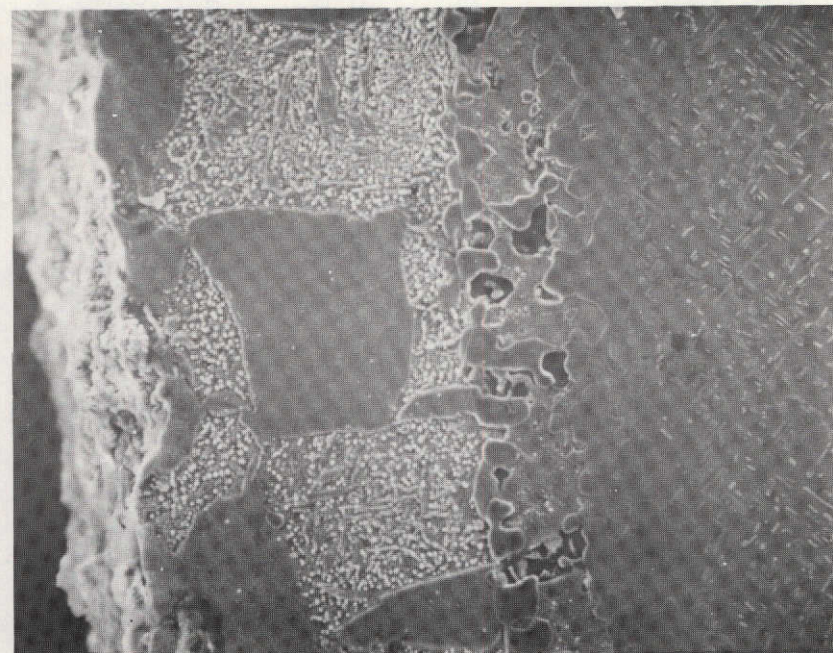


Figure 37 2X macrographs of duplex coated NiTaC-13 failed stress rupture bars. From the left, 93° to 1093°C burner rig cycled: no cycling, 871°C test; 150 hrs cycling, 871°C test; 250 hrs cycling, 871°C test; no cycling, 1093°C test; 150 hrs cycling, 1093°C test; and 250 hrs cycling, 1093°C test.



(a)



(b)

Figure 38 Longitudinal section through a stress rupture bar of duplex coated NiTaC-13 previously cyclically oxidized (93° to 1093°C in a burner rig) for 150 hrs and tested at 1093°C/110.2 MN/m²/49.89 hrs life. (a) 400X, (b) 1000X.

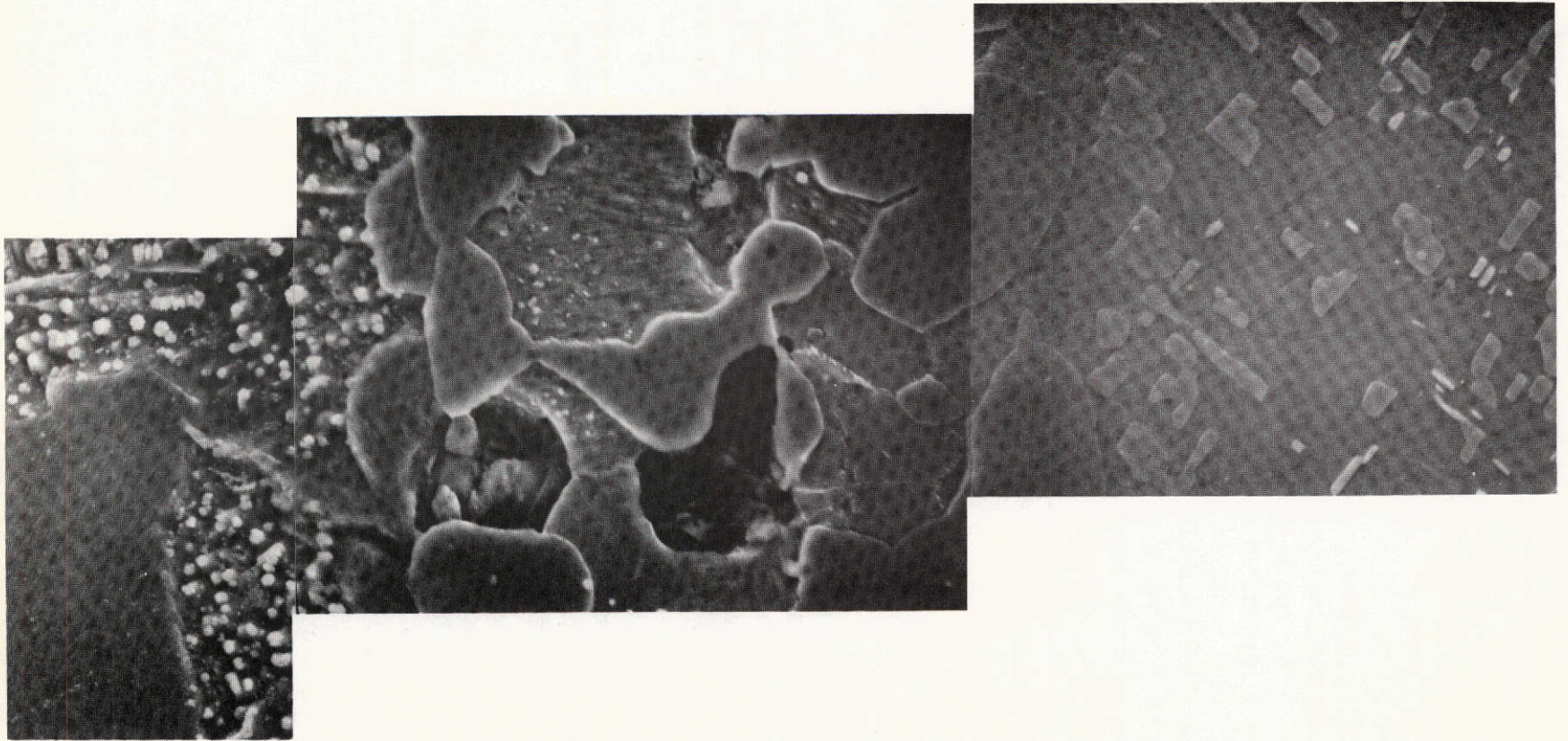


Figure 38 (continued) (c) 4450X micrograph showing features of the duplex coating.

1093°C, however, a substantial rise in stress occurred. The tensile strength reported here is that recorded at 0.05 cm/cm/min. No attempt was made to measure yield strength because of the variability from curve to curve.

Table VII contains results of the tensile tests. Stresses are calculated using final diameters for bare bars, and original (uncoated) diameters for coated bars. The room temperature ultimate tensile strength for bare NiTaC-13 was measured as 1140 MN/m². Previous measurements at AEBG (Evendale, Ohio) resulted in a value of greater than 1378 MN/m².⁽⁹⁾ If this value is used, then for all three test temperatures, independent of whether bars are coated or uncoated, the ultimate tensile strength tends to decrease with increasing cycle time. At room temperature, duplex coated samples are stronger than NiCrAlY coated bars, but at 871° and 1093°C, there is no difference. For coated cycled bars, room temperature strength and 871°C strength are essentially identical.

At room temperature, elongation and reduction of area tend to be lower for coated than for uncoated, but the correlation is not strong. At 871° and 1093°C, there is so much variation that no correlation can be drawn.

Macrographs of uncoated, NiCrAlY coated and duplex coated bars in different conditions are shown in Figs. 39 through 41, respectively. Substantial coating cracking occurred at 871°C for the 150 hours cycled NiCrAlY coated bar. This was the only test which exhibited coating cracking for NiCrAlY. For the duplex coated bars, no coating separation was seen in 1093°C testing, but coating fracture occurred in three of four tests each at room temperature and 871°C. The 150 hours cycled room temperature test and the 250 hours cycled 871°C test both show coating loss over nearly 50% of the gauge length. The 150 hours cycled 871°C test shows loss of the coating right at the fracture surface.

Figure 42a shows the microstructure of the duplex coating on a room temperature tensile test. A crack is seen running through the center of the coating parallel to the substrate. On test bars where coating loss is seen, the inner section of the coating still remains. Figure 42b shows the same behavior on a duplex coated oxidation pin burner rig cycled 250 hours. The cracking occurs in the Cr-rich phase, which is probably α Cr (~65 a/o Cr) measured by electron microprobe analysis.

Figure 43 shows the NiCrAlY coating (burner rig cycled 150 hours) on a room temperature tensile bar. The coating shows excellent bonding to the substrate. A crack is also seen running through both the substrate and coating. In the substrate, the crack follows the platelet phase.

TABLE VII

Effects of Cyclic Burner Rig Exposure (93° to 1093°C)
on Tensile Behavior of Coated and Bare NiTaC-13

	Hours of Cyclic Exposure/Coating	UTS (MN/m ²)	% Elongation	Reduction of Area
Room Temperature Tests	- / -	1140	10.8	12.1
	48 / -	1382	21.5	13.8
	48 / -	1359	16.1	16.4
	100 / -	1279	10.9	9.0
	150 / -	911	7.2	11.4
	150/NiCrAlY	964	3.3	4.8
	150/NiCrAlY	964	3.6	7.9
	190/NiCrAlY	917	6.2	4.8
	500/NiCrAlY	965	6.9	10.1
	150/Duplex	1142	6.1	9.7
	150/Duplex	928	4.3	5.5
	137/Duplex	1065	8.0	7.7
	250/Duplex	1237	9.2	10.1
871°C Tests	- / -	1128	12.0	20.1
	48 / -	1020	13.1	17.2
	48 / -	945	9.5	18.9
	150/NiCrAlY	1004	9.4	17.8
	150/NiCrAlY	980	7.8	3.7
	352/NiCrAlY	909	3.5	9.6
	500/NiCrAlY	962	4.8	6.5
	150/Duplex	1004	10.8	12.1
	150/Duplex	984	9.0	18.3
	250/Duplex	907	11.8	7.9
	250/Duplex	943	12.2	1.1
1093°C Tests	- / -	533	11.7	22.8
	48 / -	453	13.8	31.3
	48 / -	466	22.8	27.2
	150/NiCrAlY	451	26.3	36.4
	150/NiCrAlY	444	17.5	36.6
	190/NiCrAlY	417	11.8	14.7
	500/NiCrAlY	438	16.2	33.1
	150/Duplex	444	18.1	46.9
	150/Duplex	457	15.0	34.4
	250/Duplex	424	12.0	17.5
	250/Duplex	377	22.9	42.2

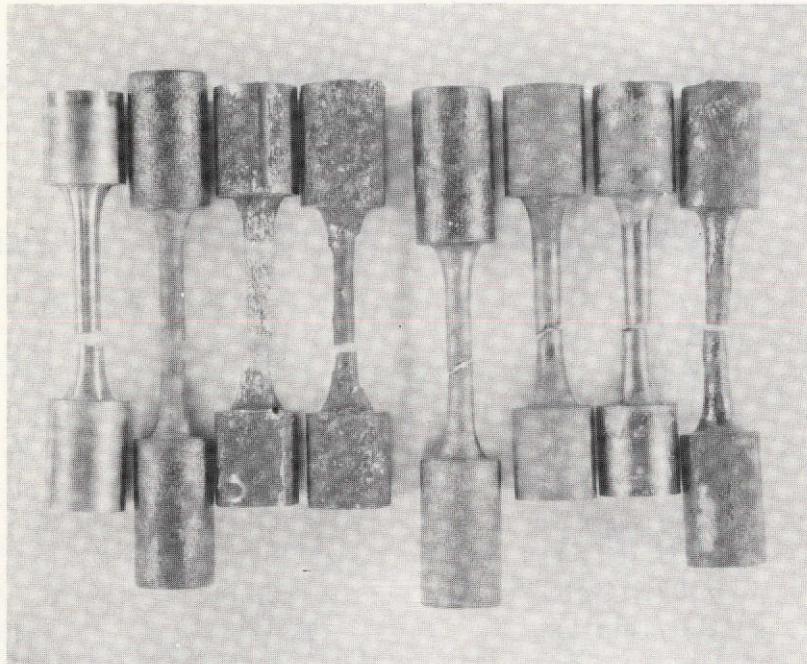


Figure 39 2X macrographs of uncoated tensile test bars after failure. From the left, burner rig cycled, 93° to 1093°C:

Room Temperature Tests	{ uncycled 48 hrs cycling 100 hrs cycling 150 hrs cycling
871°C Test	{ uncycled 48 hrs cycling
1093°C Test	{ uncycled 48 hrs cycling

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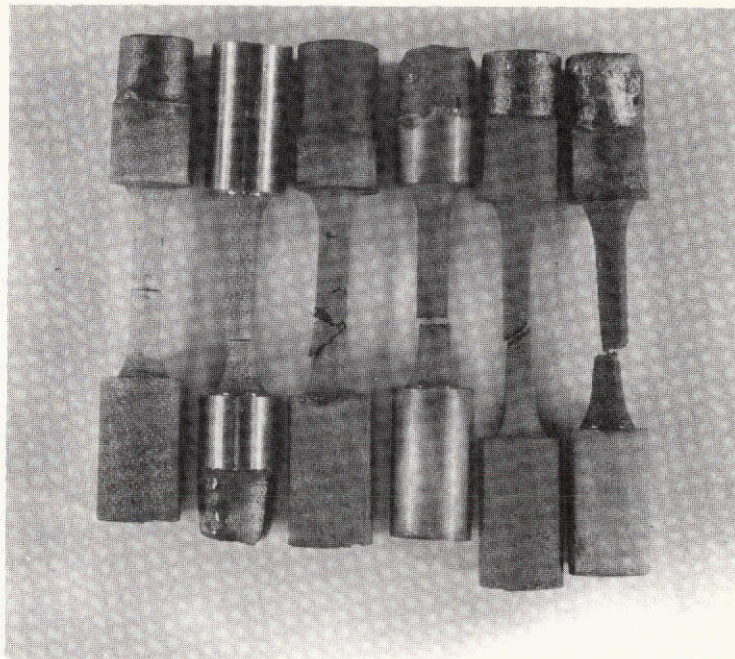


Figure 40 2X macrographs of NiCrAlY coated tensile test bars after failure.
From the left, burner rig cycled, 93-1093°C:

Room Temperature Tests	{ 150 hrs cycling 500 hrs cycling
871°C Tests	{ 150 hrs cycling 500 hrs cycling
1093°C Tests	{ 150 hrs cycling 500 hrs cycling

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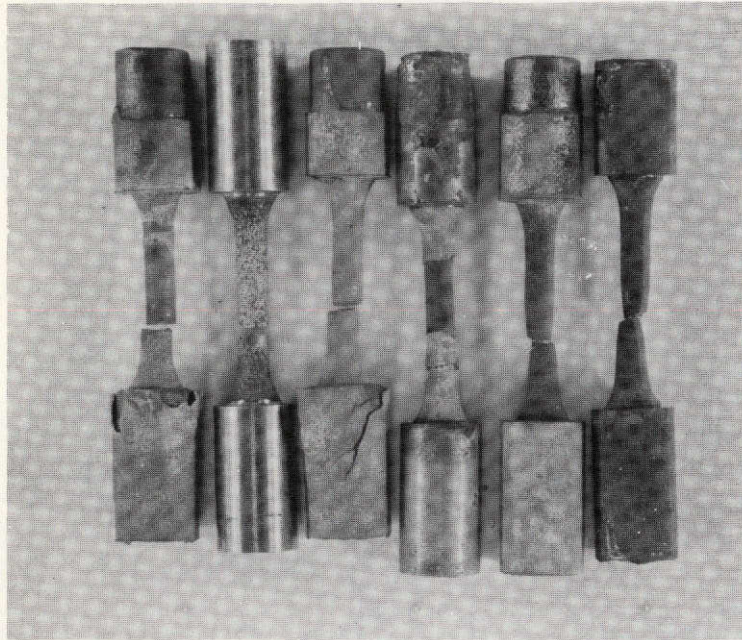


Figure 41 2X macrographs of Duplex coated tensile test bars after failure.
From the left, burner rig cycled, 93-1093°C:

Room Temperature Tests	{ 150 hrs cycling 250 hrs cycling
871°C Tests	{ 150 hrs cycling 250 hrs cycling
1093°C Tests	{ 150 hrs cycling 250 hrs cycling

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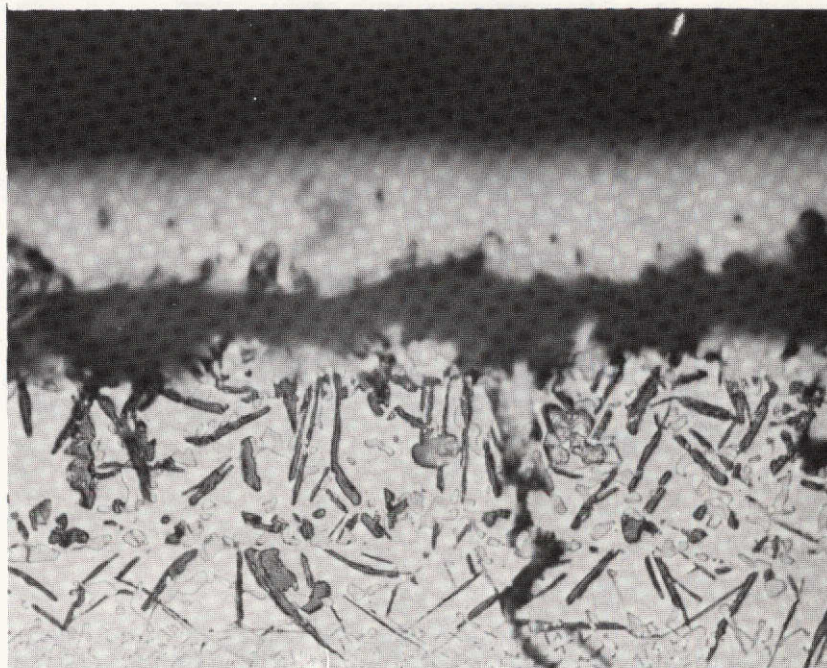


Figure 42 (a) Longitudinal section through room temperature tensile bar previously cyclically oxidized (93-1093°C in a burner rig) for 150 hours. Section is near fracture surface, showing crack running along the center of the duplex coating. Substrate is at bottom. 500X

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Figure 42 (b) Longitudinal section through duplex coated oxidation pin cyclically oxidized ($93-1093^{\circ}\text{C}$ in a burner rig) for 250 hours, showing the same features as in (a). 500X

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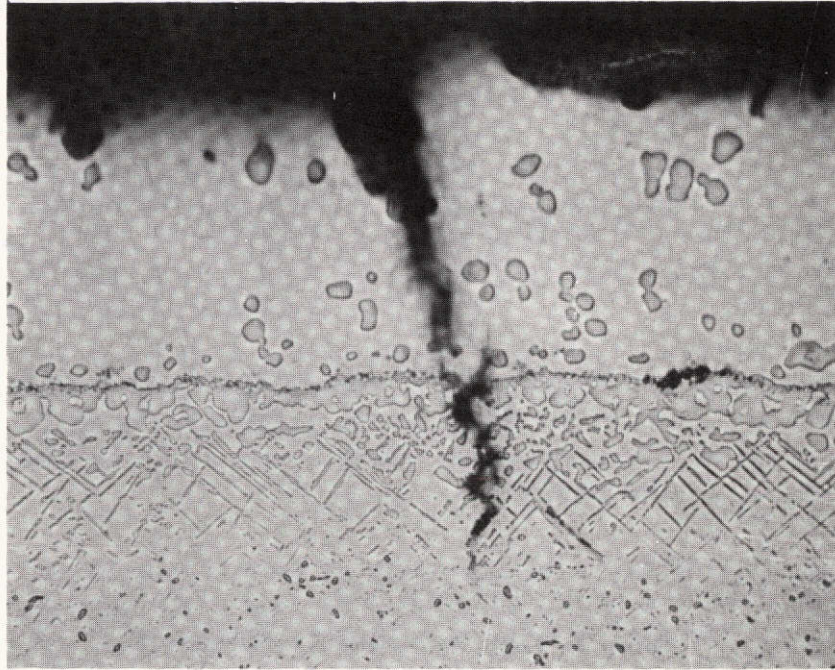


Figure 43 Longitudinal section through room temperature tensile bar previously cyclically oxidized for 150 hours. 93-1093°C in a burner rig. Section is near fracture surface, showing NiCrAlY coating is well bonded to the substrate. Crack is propagating into the substrate along platelets. 500X

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SUMMARY OF RESULTS

1. An oxidation resistant coating is necessary for NiTaC-13.
2. Of seven Co, Fe-, and Ni- base coatings studied on NiTaC-13 in cyclic (93-1093°C) furnace oxidation, Ni-20Cr-15Al-1Y and Ni-35Cr+Al are best. The NiCrAlY coating gained $\sim 6\text{mg/cm}^2$ in 348 hours of cycling, the duplex coating behaved similarly, and bare NiTaC-13 lost 250 mg/cm^2 in 163 hours.
3. Cyclic burner rig exposure (JP-5 fuel, 0.05 MACH, 93-1093°C, one-hour cycles) caused failure (measured by weight change and appearance) in 200 hours for bare samples, 630 hours for duplex coated, and 830 hours for NiCrAlY coated samples.
4. After cyclic exposure, little change is noted in the coatings, but substantial changes occur in the substrate. A platelet phase precipitates in the matrix, and the microstructure exhibits coarsening.
5. A fiber denuded zone forms at the coating-substrate interface, which grows with increasing cycle time. Denudation of fibers appeared to be a minor problem for mechanical behavior of .254 cm diameter bars. The effect may be of greater importance in thin wall (.1 cm) turbine blade sections.
6. A 10% loss in 871 and 1093°C tensile strength occurs for bare NiTaC-13 cycled 48 hours. No further detrimental effect of coatings on strength is noticed at room temperature, 871 or 1093°C.
7. NiCrAlY coatings offered excellent oxidation protection for burner rig cycled samples subsequently rupture tested at 1093°C: cycled and air tested NiCrAlY coated samples had rupture behavior equivalent to vacuum cycled and argon tested bare NiTaC-13. Cycled and air tested duplex coated samples were equivalent to vacuum cycled and air tested bare NiTaC-13 at 1093°C.
8. In 871°C air stress rupture, samples with either coating exhibited a degradation (<1 Larson-Miller parameter) relative to bare material. This was true for both cycled and uncycled conditions.
9. Ni-20Cr-15Al-1Y is a superior coating to Ni-35Cr+Al when applied to NiTaC-13.

RECOMMENDATIONS

This study has clearly demonstrated the necessity of providing an oxidation resistant coating for NiTaC-13. Further, it has been shown that substantial oxidation resistance is provided by the two nickel-based coatings studied in Task II, Ni-20Cr-15Al-1Y and Ni-35Cr+Al.

It is recommended that a follow-on program should be undertaken to further develop the coatings evaluated under this contract. This recommended program would consist of three parts:

1. The development of improved high aluminum (10-15%) NiCrAlY by eliminating or minimizing the tendency for the formation of a zone that is denuded of carbide fibers in the substrate region adjacent to the coating. This should be possible by establishing a "diffusion barrier" between the coating and the substrate; and/or, by increasing the carbon content of the coating in order to reduce the chemical potential for carbon diffusion away from the substrate.
2. The development of an improved duplex coating. For instance, an initial layer of a composition such as Ni-20Cr-5Al-1Y should be aluminized to greatly improve its oxidation resistance.
3. The development of an improved CoCrAlY by establishing an integral bond between the coating and the substrate. An added metal layer should be used to achieve this bond.

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